Applicants: Donald R. Huffman, et al.

Serial No.   08/471,890

Docket: 7913ZY

Filing Date: June 7, 1995

Examiner: S. Hendrickson

Group Art Unit: 1754

Title: DECLARATION OF RAOUF O. LOUTFY

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s): Donald R. Huffman, et al.   Examiner: Hendrickson

Serial No.: 07/580,246   Art Unit: 1754

Filed: September, 10th 1990   Docket: 7913Z

For: NEW FORM OF CARBON

Assistant Commissioner for Patents
Washington, DC 20231

DECLARATION OF Raouf O. Loutfy

I, Raouf Loutfy, hereby declare:

1.   I reside at 6507 N. Ventana Canyon Drive, Tucson, Arizona, USA.

2.   I earned a B.Sc. degree in 1964 in Applied Chemistry from Cairo University, a M. Sc. in 1966 in Solid State Sciences from the American University, a Ph.D in 1971 in Physical Chemistry from University of Western Ontario, and a Diploma in Business Administration in 1976 from McGill University.

3.   Between 1977 and 1981 I was employed as a group leader at Argonne National Laboratory in the Chemical Engineering Division.

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4.   Between 1981 and 1985 I was employed as Research Advisor of ARCO Metals/ARCO Chemical developing advanced material technologies.

5.   Between 1985 to present I have been employed as president of MER Corporation, and since 1990 I have been involved in the commercial scale-up of fullerenes, and in developing applications for fullerenes.

6.   I have published many articles, two books, and contributed a chapter in Encyclopedia of Technology on the fullerene production, and on applications of fullerenes. I have been an invited speaker to many technical and investment conferences as an expert in the technology and commercialization of fullerenes. I have received the prestigious Tibbetts award in 2001 from the Small Business Administration (SBA) for the commercialization of fullerenes.

For the convenience of the patent and trademark office, I have attached hereto as Exhibit 1 my curriculum vitae, which describes my credentials and demonstrates my expertise in the area of fullerenes.

7.   I am intimately familiar with the published literature concerning fullerenes and I am personally involved in the research and development of new methods of production and applications for fullerenes including C_{60}, C_{70} and nanotubes.

8.   I am informed by Mark J. Cohen, Esq., the attorney handling the prosecution of the subject United States patent application that a question has arisen concerning the use

of the term "macroscopic amounts" as applied to the fullerene products, e.g. C_{60} and C_{70} that are produced by the methods invented by Drs. Huffman and Kratschmer as described in the underlying application.

9.   As set forth above, I have been professionally involved in the field of fullerenes development and manufacture since Dr. Huffman and Kratschmer disclosed their novel process for producing macroscopic quantities, i.e., visible quantities of fullerenes, e.g., C_{60} and C_{70}, as disclosed in the subject patent application and in their publication in Nature (1990) identified elsewhere in this Declaration and I am familiar with the use of the term "macroscopic quantities" in this field and, in general, in the scientific and academic communities.

10.   I have read and reviewed the subject patent application, including the pending claims. It is my understanding that the subject application discloses, among other things, a process of producing fullerenes including C_{60} and C_{70} in macroscopic amounts and that, inter alia, U.S. Serial No. 07/580,246 includes claims directed to macroscopic quantities of C_{60} and C_{70}.

11.   Although the subject patent application of Dr. Kratschmer and Huffman does not expressly use the term "macroscopic amounts" to describe the amounts of fullerenes, e.g., C_{60} and C_{70} first isolated by them, in accordance with the teaching of the process described therein, the fullerenes, e.g., C_{60} and C_{70}, that were prepared in accordance with the process described herein, were produced in measurable amounts that were visible to

them, and it is my professional opinion that these amounts are inherently amounts definable by the term "macroscopic amounts".

12.   Part of our research and development at MER involves the use of various arc processes, plasma processes, and high temperature process to produce fine metal, ceramic, and carbon powders. In the course of this research and development work, MER has since from about 1985 to the present maintained equipment and capabilities that could have produced soot. I am quite familiar with the principal of operations and the use of such equipment. At MER, I regularly produced soot under arc, plasma, and high temperature conditions for various applications. I am also familiar with the work of the Nobel Laureate Sir Harry Kroto et al. al. published in Nature volume 318, No. 6042, 14-20 November 1985. p162. In this publication they report the detection of remarkably stable cluster of 60 carbon "atom" using time-of-flight mass spectrometry in the vapor phase. However, they never isolated or recovered visible particle of C_{60} and C_{70}, and did not disclose a process that would teach or lead others to do so. It is noted they reported the following "If a large-scale synthetic route to this C_{60} species can be found, the chemical and practical value of the substance may prove extremely high".

13.   On or about September 18, 1990, MER received and executed confidentiality agreement from RCT regarding disclosure to MER of Huffman's et al. al. discoveries.

14.   . On or about September 20, 1990, Dr. Huffman of U of A and Mr. Jacobs of RCT visited MER Corporation to further discuss proactive strategy concerning an arrangement

to license from RCT under the Huffman et. al. invention to produce fullerenes at MER and to capitalize on the fullerene discovery of Dr. Huffman et al., and to discuss in details the production and the separation of fullerenes from the vaporized carbon utilizing the Huffman et al. discoveries.

15.   On October 9, 1990, Dr. Withers, CEO of MER, and I visited Dr. Huffman's laboratory and observed his apparatus and witnessed the operation of his apparatus for vaporization of carbon, and production and collection of soot containing fullerenes. In many respects, Dr. Huffman's apparatus was very similar to much of the equipment at MER; however, MER had not used their equipment to produce fullerenes prior to the Huffman et. al. invention. The operating conditions for such equipment and the realization of the existence of fullerenes in the soot were the missing elements, not only from MER's viewpoint, but also from that of all other researchers prior to the Huffman et. al. invention. The equipment of MER and others will not produce inherently fullerene and even if produced it was not known that it could be recovered as it was later taught by Dr. Kratschmer and Huffman. All researchers in this field either produced soot under high vacuum conditions, without sufficient concentration of carbon vapor, at low pressure, or without sufficient cooling or combination of these conditions to produce recoverable fullerenes in the soot. These conditions resulted in product that does not contain fullerenes. Even though it appears simple to the uninformed, especially in hindsight, the process of Dr. Kratschmer and Huffman as described in the subject application, is a remarkable discovery, which produced a high density of vapor of carbon as described on page 4 of the subject application which resulted in the formation of

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macroscopic amounts of fullerenes by their method. From 1985, when Dr. Smally et. al. at Rice University discovered the existence of C_{60} and C_{70} atoms by spectrographic analysis of a vapor (see paragraph 12 above), until Dr. Huffman et. al. published their discovery in 1990 no one else realized how to produce and recover macroscopic quantities of these fullerenes, despite the availability of equipment that could have been used for this purpose.

16.   I directed experiments to produce fullerene soot at MER using equipment at MER, and we also built additional low vacuum equipment based on the Kratschmer and Huffman method described in the subject application and produced macroscopic quantities of soot and fullerene. We separated the fullerene according to their teaching. From a similar apparatus as that described in the subject application, but operated for sufficient time, we were able to offer for sale to the research community fullerenes including pure (90%+) C_{60} and C_{70} by November 1990.

We have since developed computer control, fully automated reactor equipment using Kratschmer and Huffman's teaching in the subject application and we optimized the process to maximize the yield of fullerenes.

17.   I repeated exactly the Huffman et. al. process according to the teaching described in the subject application including example 1 using ¼ inch in diameter graphite rod, at 100 torr Helium, using 100 ampere dc current. This graphite vaporized, and the vapor was condensed on a water cooled surface. The vaporization was performed for 50 minutes using about 17 cm length of the graphite rod and produced 12 gram of soot. The

fullerenes were recovered using tolerene and the amount of fullerene was determined. The yield of fullerene was about 8 to 10%. Accordingly, the total recoverable fullerenes was over 1.2 grams with over 900 mg of C_{60} and over 200 mg of C_{70} and the remaining other fullerenes.

According to the teaching in the subject application where they vaporized a ¼" graphite rod with 1 cm length, the inventor must have produced at least about 600 mg of soot that contains admixture of at least 63 mg of fullerenes that contain at least about 50 mg of C_{60} and at least about 10 mg of C_{70}. A 600-mg quantity of soot certainly can be seen by the naked eye, as also indicated by the inventor that "heavy block coating on collecting substrates and/or on the walls of the chamber which can be easily scraped off for the recovery step." Also, the 60 mg of fullerene certainly can be seen by the naked eye and it is measurable. Furthermore, the 45 and 10 mg of C_{60} and C_{70} respectively are also measurable, in today modern laboratory facility amount as low as 0.1 mg can be measured, and can be seen by the naked eye.

The same conclusion can be reached by simply calculating the mass of the rod vaporized in Kratschmer et al. subject application, including example 1, which is easily determined from the diameter of the graphite rod they used (1/4"), the length (1 cm), and typical density of the type of graphite used for graphite vaporization (2.0 g/cc). This calculation estimates that about 633 mg of soot containing fullerenes was produced by Kratschmer et al., which is certainly macroscopic and in agreement with the above-presented experimental data.

Moreover, if a longer graphite rod were used, the amount of C_{60}, C_{70} and other fullerenes produced would even be greater, as shown herein above.

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18. It is in my opinion that the inventors of this subject application were the first to isolate and recover a measurable or macroscopic amount of fullurenes, and to teach others to do so. Their description in the application is clearly understood by ordinary skilled artisans, and when repeated by us allowed us to produce visible, measurable commercial quantities of fullerene product, commonly described as "macroscopic quantities".

19. It is also in my opinion that the inventors produced "macroscopic amounts" as used in the claims as clearly understood by the ordinary skilled artisan, and supported by the above. The term is commonly used to connote that amount which can be seen easily with the naked eye. This opinion is corroborated by the usage of this term by others in the fullerene field to describe the fullerene product produced by the process invented by Drs. Kratschmer and Huffman, for example, see the statement appearing at Column 1, lines 58-61 in U.S. Patent No. 6,077,401 issued June 20, 2000, on an application filed August 15, 1994, which is as follows:

"All of these applications have been discovered since the first

macroscopic amounts of the most common fullerene, C_{60},

were isolated in 1990 [Kratschmer, et al., Nature 347, 354 (1990)]."

The cited quote from the Fields et. al. patent also corroborates the common understanding of those familiar with the fullerene art that they were the first persons to produce fullerenes in macroscopic quantities and to show others how to do so.

For the convenience of the patent and trademark office, I have attached hereto as Exhibit 2 the cited patent.

I further declare that all statements made herein of my own knowledge are true, and all statements made on information and belief are believed to be true. I acknowledge that willful false statement and the like are punishable by fine or imprisonment or both (18 U.S.C. §1001) and may jeopardize the validity of the application or any patent issuing thereon.

July 16, 2002
Date

Raouf O. Loutfy, Ph.D

Signed in Tucson, Arizona

Exhibit # 1

Curriculum Vitae of Dr. RAOUF O. LOUTFY

EDUCATION

Diploma   Business Administration, McGill University, 1976
Ph.D.   .   PhysicalChemistry/Electrohemistry, University of Western Ontario, 1971
M.Sc.   Solid State, American University, 1966
B.Sc.   Applied Chemistry, Cairo University, 1964

PROFESSIONAL EXPERIENCE

1999 – Present   COO, FIC Corporation, New York, NY
Responsible for technical direction of this joint venture between MER, Mitsubishi Corporation, and RCT Corporation for the commercialization of Fullerene and Fullerene based materials.

1985 – Present   President, MER Corporation, Tucson, Arizona
Responsible for developing advanced programs and technologies, managing research and development group, contract administration and financial responsibilities. Produced SiC whiskers, SiC Fibers, ceramic-ceramic composites, advanced lithium-ion battery technology, low cost bipolar plates for fuel cell. Lead a group to develop scale-up production of fullerenes, and its applications development.

1986 - 1988   President, Keramont Research Corp., Tucson. AZ
Responsible for building the infrastructure (equipment, personnel, and projects) for advanced materials research organization with emphasis on electronic ceramics, aluminum nitride substrates reinforcements (SiC_w, SiC_f and $TiB2_w$) and composites (ceramic-ceramic, and metal-ceramic. and intermetallic ceramic).

1981 - 1985 Research Advisor, ARCO Metals/ARCO Chemical Company, Tucson. AZ
Major responsibility in the development of advanced technology to produce primary light metals and advanced materials, and to provide company-wide support in area of expertise. These efforts result, amongst others, in a commercial plant for the production of high purity alumina.

1977–1981   Group Leader, Chemical Eng. Div., Argonne National Laboratory, IL
The major responsibility, as a group leader of the Electrolytic Technology Research Group, was to develop and implement a plan for the electrochemical technology for energy and resource saving. This was achieved by supporting and conducting research and development to improve industrial processes and identifying and developing new concepts of low energy alternative technologies. A second responsibility is the technical management of contracts in the electrolytic area and contracts for developing batteries for load-leveling applications.

1972-1977   Group Leader, Noranda Research Center, Pointe Claire, Quebec
In charge of developing advanced pyro metallurgical and electrometallurgical processes to improve plant operations and profitability. Those efforts led to the development of DSA anodes for metal winning, and a new oxidant for zinc purification process.

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AWARDS

TITLE OF AWARD	DATE	PRESENTED BY	REASON FOR AWARD
Industrial R&D 100	1990	R&D Magazine	Development of SiC Fibers
Corporate Entrepreneur of the year	1990	AIN	Most Number of Contract Won in Arizona
Industrial R&D 100	1991	R&D Magazine	Development of SiC Whisker
Product of the Year	1991	AIN	Fullerenes Production
Industrial R&D 100	1996	R&D Magazine	PDS Powder
Tibbetts Award	1998	SBA	SBIR Commercialization
Tibbetts Award	2001	SBA	Commercialization of Fullerene

PUBLICATIONS AND PATENTS

- 24 U.S. patents (12 have been in the last 10 years)
- 12 patent disclosures
- 90 articles published
- A chapter on Hydrogenated Fullerene in the Encyclopedia of Technology
- 2 books, both on Fullerenes:

D. Koruga, S. Hameroff, J. Withers, R.O. Loutfy, and M. Sundareshan "Fullerene, C60: History, Physics, Nanobiology, and Nanotechnology" Elsevier Science Publishing Co. New York, NY 1993.

"Perspectives of Fullerene Nanotechnology", edited by Eiji Osawa, Kluwer Academic Publishers, February 2001.

The specific Chapters are:

1. R.O.Loutfy, A. Moravsky, A. Franco, and E.Veksler "Physical Hydrogen Storage on Nanotubes and Nanocarbon Materials"
2. R.O.Loutfy, S.Katagiri "Fullerene Materials for Lithium-ion Battery Applications"
3. R.O. Loutfy, S. Hossain, A. Moravsky and M. Saleh "Nanotubes as Anode Material for Lithium-ion Batteries"
4. Raouf O. Loutfy and Eugene M. Wexler "ABLATIVE AND FLAME-RETARDANT PROPERTIES OF FULLERENES"
5. R.O. LOUTFYJ. C. WITHERS, AND M. ABDELKADER "Development of Carbon Nanotube - Polymer Composites"
6. Raouf O. Loutfy, J.C.Withers and Stevan T. Dimitrijevic "USE OF FULLERENES AND CARBON NANOTUBES FOR FABRICATION OF EFFICIENT ELECTRON FIELD EMITTERS"
7. Raouf O. Loutfy, Eugene Weksler, and Weijiong Li "UNIQUE FULLERENE-BASED HIGHLY MICROPOROUS CARBONS FOR GAS STORAGE"
8. Raouf O. Loutfy, Timothy P. Lowe, Alexander P. Moravsky, and S. Katagiri "Commercial Production of Fullerenes and Carbon Nanotubes"
9. Raouf O. Loutfy, Eugene Weksler "GAS PHASE HYDROGENATION OF FULLERENES"

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10. Raouf O. Loutfy, Eugene Weksler "HYDROGENATION OF ALKALI METAL – DOPED FULLERENES"
11. R.O.Loutfy, and M.Hecht "Aligned Carbon-Nanotubes for Sensor Applications"
12. Raouf O. Loutfy, Eugene Weksler "ADVANCED THERMAL PROTECTION COATING USING FULLERENES"

Other Fullerenes Publications:

S. Seraphin, J.C. Withers, R.O.Loutfy, et al, "TEM Studies of Nanotubes and Graphite Particles", Symposium of the Arizona Fullerene Consortium, November 6, 1992.

S. Seraphin, J.C. Withers, et al, "TEM Study of Carbon Nanotubes Produced by Various Processing Conditions," to be presented a John M. Crowley Symposium, Arizona State University, January 5-8, 1993.

S. Seraphin, J.Jiao, D. Zhou, J.C. Withers, R.O. Loutfy, "Effect of Processing Conditions on the Morphology and Yield of Carbon Nanotubes," *Carbon*, Vol 31, No 5, 685 (1993).

S. Seraphin, J. Jiao, D. Zhou, J.C. Withers, R.O. Loutfy, "Yttrium Carbide in Nanotubes," *Nature*, Vol. 362, April 8, 503 (1993).

J.C. Withers, R.O. Loutfy, K.Y. Donaldson, D.P. Hasselman, "Thermal Diffusivity/Conductivity of Compacts of C_{60} Buckminsterfullerene and a C_{60}/C_{70} Mixture, "*J.Am. Cerm. Soc.*, Vol 76, No 3, 754 (1993).

D. Koruga, J.S. Kustic, M. Trifunovic, S. Jankovic, S. Hameroff, J.C. Withers, R.O. Loutfy, "Imaging Fullerene C_{60} with Atomic Resolution Using a Scanning Tunneling Microscopy", *J. of Full. Science & Technology*, Vol 1, 93 (1993).

R.O. Loutfy, J.C. Withers, "Fullerene & Electrochemical Hydrogen Storage" abstract 2145, Electrochem. Soc. Mtg, Hawaii, (1993).

J.C. Withers, R.O. Loutfy, "Production Process for Fullerenes, Review" Abstract #2127 Electrochem. Soc. Meeting, Hawaii (1993).

T. Yadav, S. Seraphin, D. Zhou, J.C. Withers, R.O. Loutfy, "Catalytic Growth of Buckyonions," in preparation

S. Supapan, D. Zhou, J.Jiao, M. Minke, S. Wang, T. Yadav, J.C. Withers, R.O. Loutfy, "The Effect of Pt, Pd and Ni on the Synthesis of Carbon Clusters," in preparation

J.C. Withers, C. Pan, R.O. Loutfy, "Fullerene Price: How Low Will They Be?" Electrochemical Society Mtg., San Francisco, Abstract 1216, (1994)

Contracts

3

DOE contract #DE-FG02-92ER81272, "The Development of a Process to Synthesis Tubular Fullerenes", Phase II, July 92

DOE contract #DE-FG02-91ER81095, "Novel C_{60} Electrodes for Advanced Electrochemical Sensors", Phase I, Sept 91.

ARMY contract #DAAH04-93-C-0004, "Novel Materials for Hydrogen Supplies and Storage for Fuel Cells, Phase I, Jan 93.

ARMY contract #DASG60-93-C-0003, "Use of High Energy Lasers for Materials Synthesis", Phase I, Nov 92.

NASA contract #NAS5-32430 Goddard, "A Novel Negative Hydride Electrode for Ni-Metal Hydride Batteries", Phase I, Dec 92.

Exhibit #2

Exhibit2

US006077401A

United States Patent [19]

Fields et al.

[11] Patent Number: 6,077,401

[45] Date of Patent: Jun. 20, 2000

[54] PRODUCTION OF FULLERENES USING CONCENTRATED SOLAR FLUX

[75] Inventors: Clark L. Fields, Greeley; John Roland Pitts; David E. King, both of Lakewood; Mary Jane Hale, Golden; Carl E. Bingham, Denver; Allan A. Lewandowski, Evergreen, all of Colo.

[73] Assignee: Midwest Research Institute, Kansas City, Mo.

[21] Appl. No.: 08/290,538

[22] Filed: Aug. 15, 1994

[51] Int. Cl.[7] C01B 31/02
[52] U.S. Cl. .... 204/157.47; 423/445 B; 423/445 R
[58] Field of Search .... 423/445 B, 445 R; 204/157.47

[56] References Cited

U.S. PATENT DOCUMENTS

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5,128,115	7/1992	Glatzmaier	23/295 S
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OTHER PUBLICATIONS

Smalley, R. "Self-Assembly of Fullerenes", Accounts of Chem. Research, vol. 25, #3, pp. 98-105, Mar. 1992.
Howard, et al., Nature, 352, 139 (1991).
H. Kroto et al., "C60: Buckminster Fullerene", Nature 318, 162 (1985).
Kratschmer, et al., Nature, 347 354 (1990).

J. Phys. chem. 97 (34), 8701 (1993), Chibante et al.
Fields, C.L., et al. "Formation of Fullerenes in Highly Concentrated Solar Flux", J. Phys. Chem., vol. 97 (Aug. 26, 1993) pp. 8701-8702.
IBM Technical Disclosure Bulletin, vol. 34, #4B, Sep. 1991, p. 222, Entitled "Method for Mass Producing Large 'Fullerene' Type Carbon Clusters Using Localized Heating Sources".
Diederich, F., et al. Science, vol. 254, pp. 1768-1770 (Dec. 20, 1991), Entitled "Fullerene Isomerism ...".
McKinnon, J.T. "Calculated Equilibrium Yields of (60 From Hydrocarbon Pyrolysis ..", J. Phys. Chem., 1991, vol. 95, pp. 8941-8944.

Primary Examiner—Michael Lewis
Assistant Examiner—Peter Di Mauro
Attorney, Agent, or Firm—Ken Richardson

[57] ABSTRACT

A method of producing soot containing high amounts of fullerenes comprising: providing a primary concentrator capable of impingement of a concentrated beam of sunlight onto a carbon source to cause vaporization of carbon and subsequent formation of fullerenes, or providing a solar furnace having a primary concentrator with a focal point that concentrates a solar beam of sunlight; providing a reflective secondary concentrator having an entrance aperture and an exit aperture at the focal point of the solar furnace; providing a carbon source at the exit aperture of the secondary concentrator; supplying an inert gas over the carbon source to keep the secondary concentrator free from vaporized carbon; and impinging a concentrated beam of sunlight from the secondary concentrator on the carbon source to vaporize the carbon source into a soot containing high amounts of fullerenes.
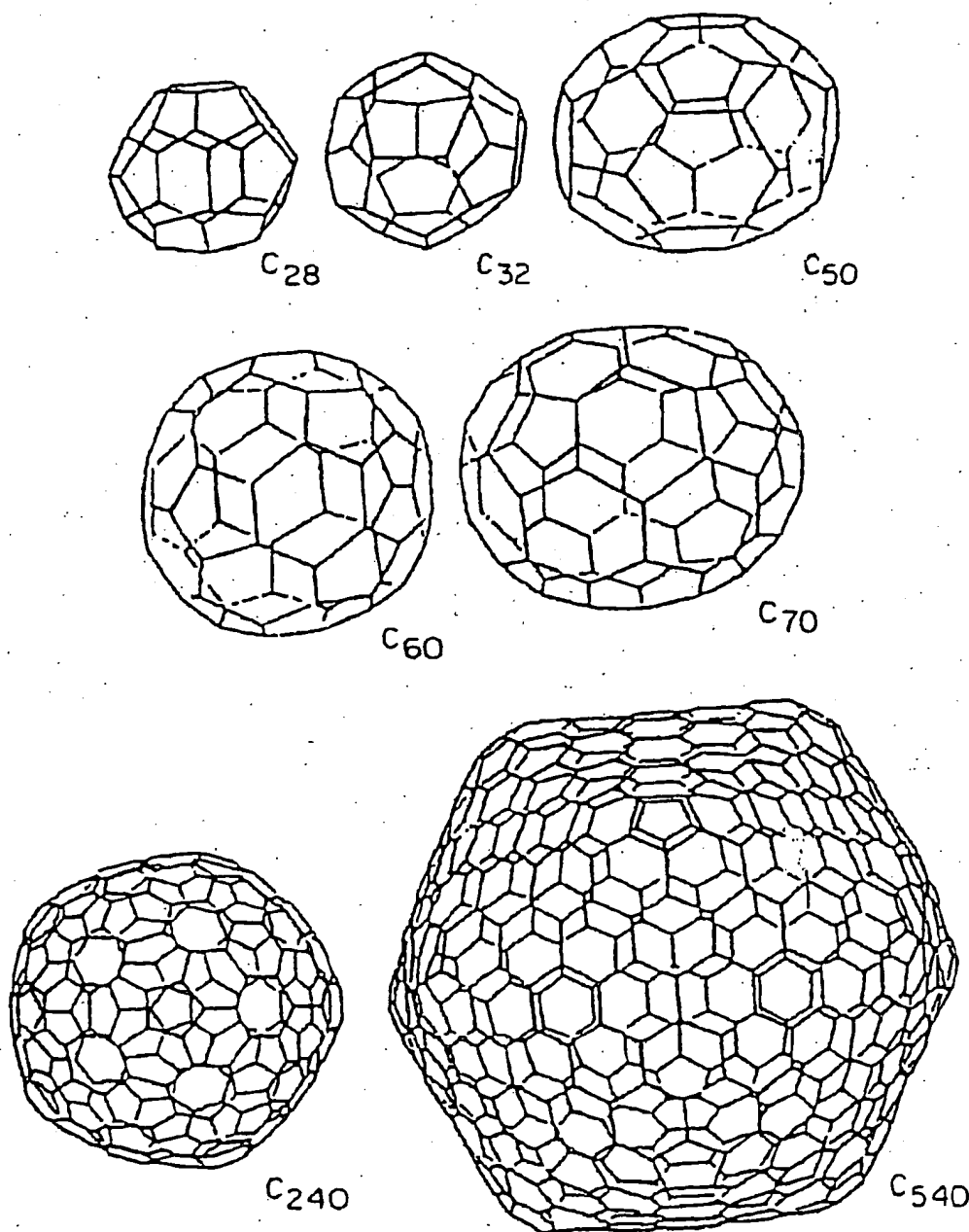
20 Claims, 6 Drawing Sheets
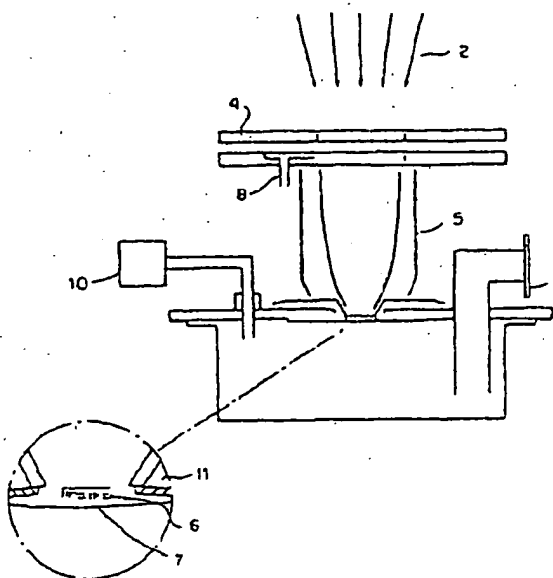
FIG.1

C_{28} C_{32} C_{50}

C_{60} C_{70}

C_{240} C_{540}

FIG.2

FIG.3

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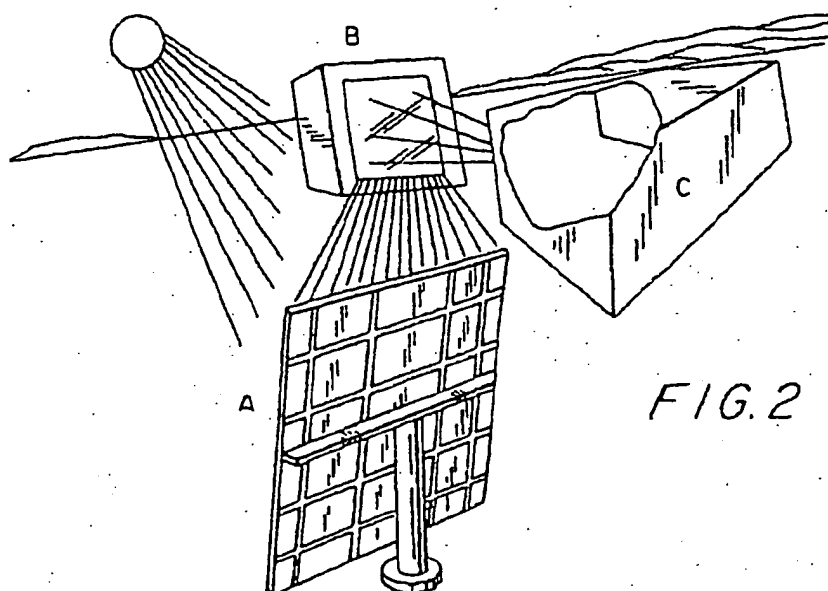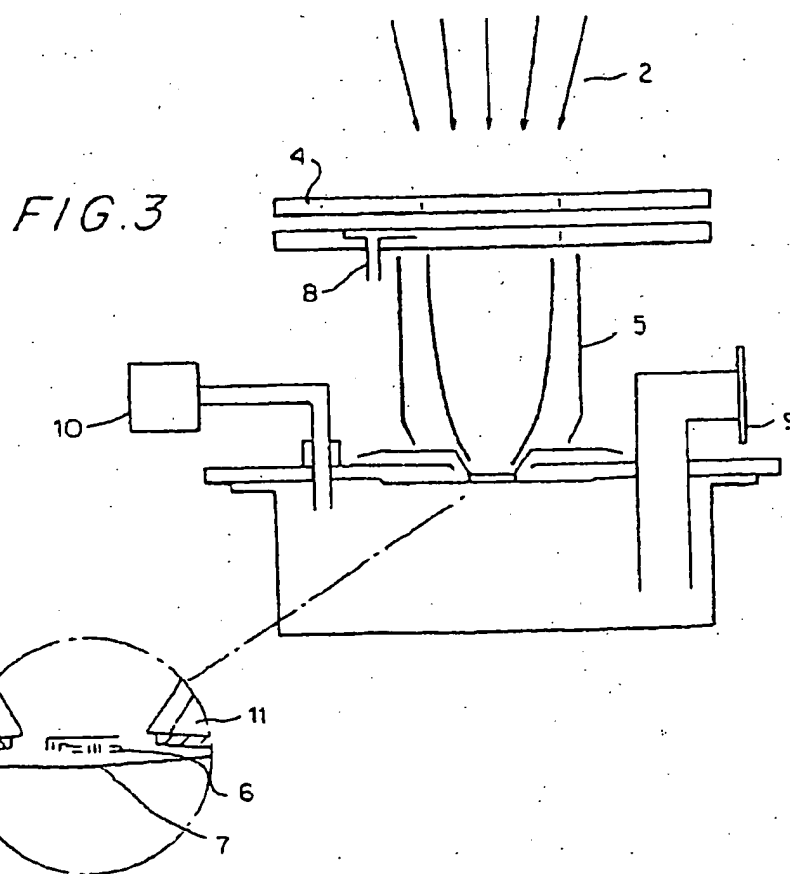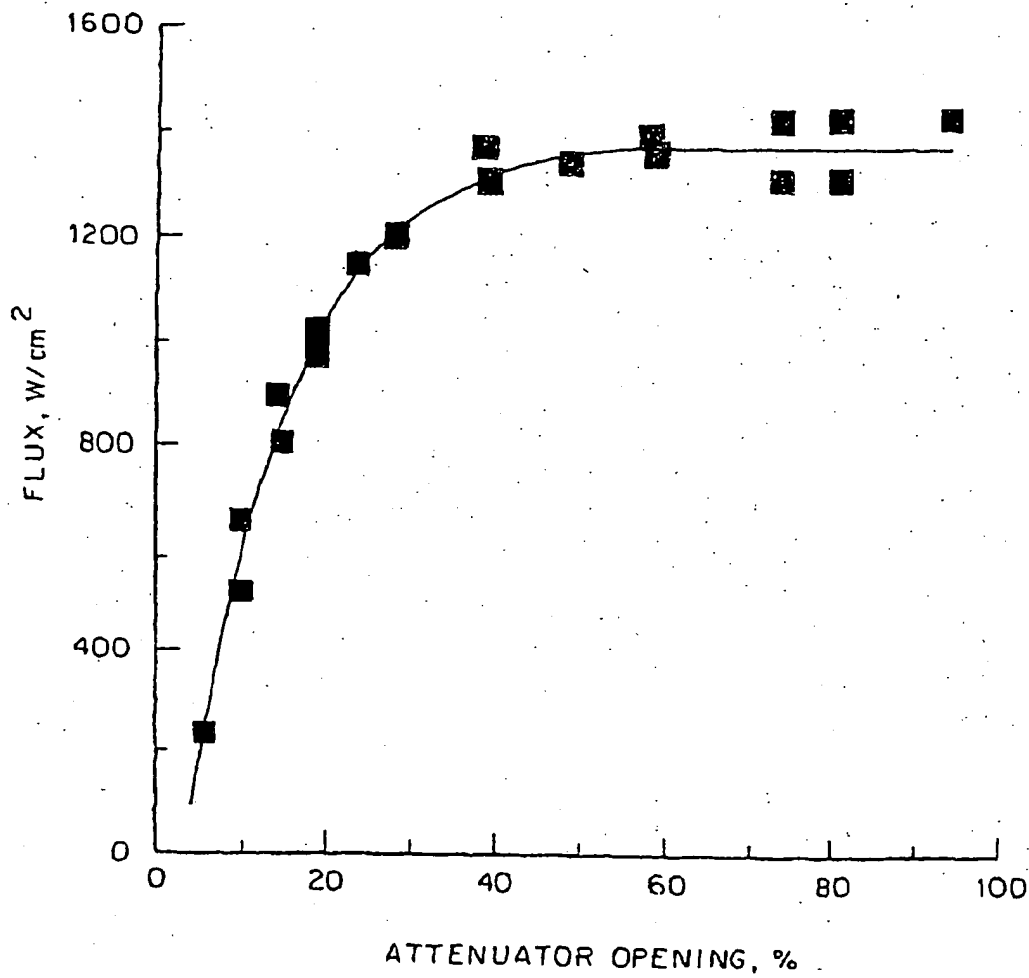
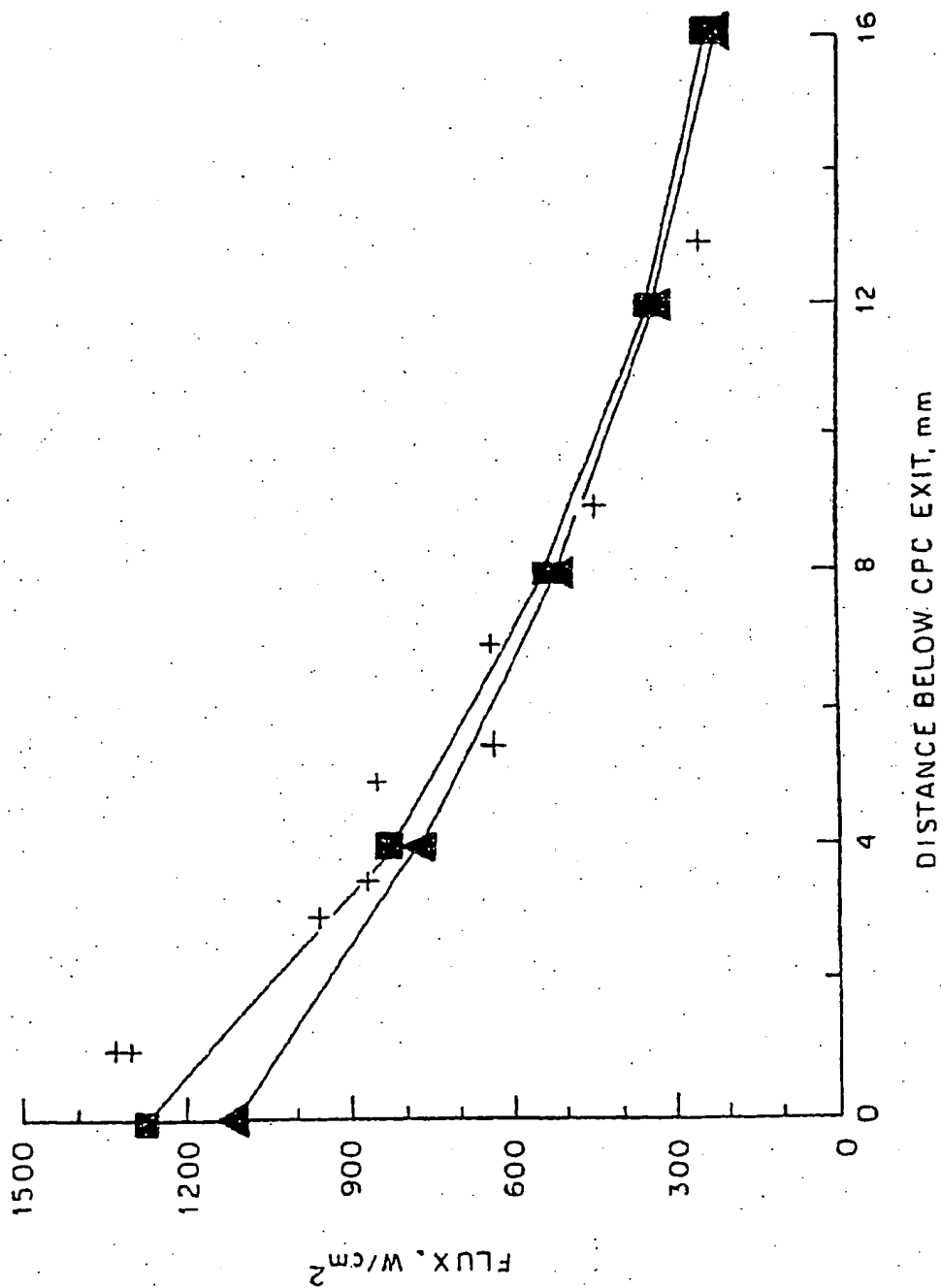*F I G. 4*

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FIG. 5

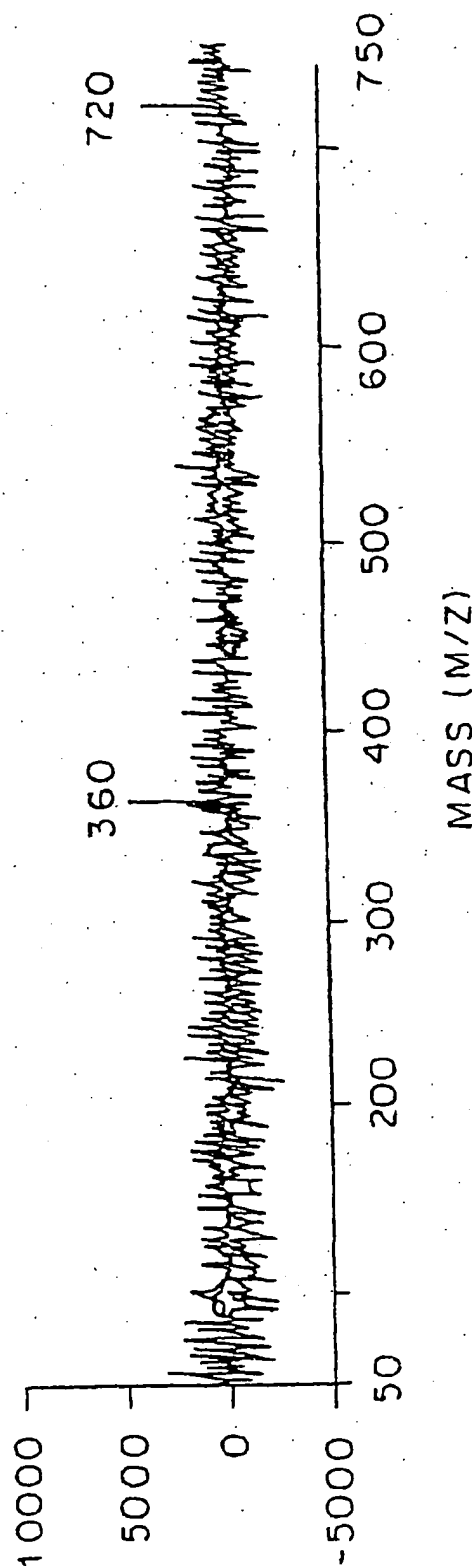**U.S. Patent**   Jun. 20, 2000   Sheet 5 of 6   **6,077,401**

FIG. 6

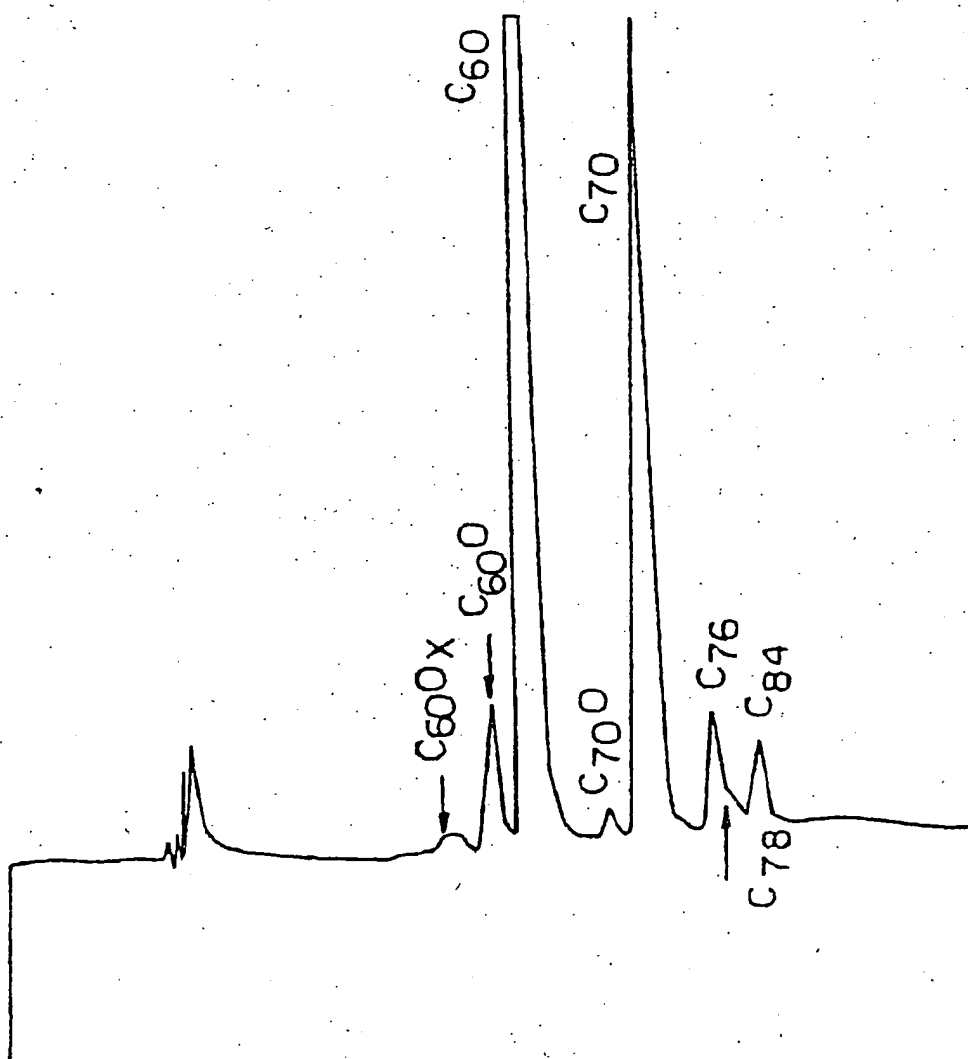U.S. Patent   Jun. 20, 2000   Sheet 6 of 6   6,077,401

F I G. 7

6,077,401

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PRODUCTION OF FULLERENES USING CONCENTRATED SOLAR FLUX

The United States Government has rights in this invention under Contract No. DE-AC02-83CH10093 between the United States Department of Energy and the National Renewable Energy Laboratory, a Division of the Midwest Research Institute.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates generally to a process for delivering highly concentrated solar radiation to a material surface to evaporate the material so that it condenses into caged molecules.

More specifically, the invention is directed to a method for producing fullerenes by: providing a solar furnace having a focal point wherein the solar furnace concentrates sunlight; providing a reflective secondary concentrator having an entrance aperture and an exit aperture at the focal point of the solar furnace; providing graphite at the exit aperture of the secondary concentrator; flowing argon gas over the graphite to keep the secondary concentrator free from vaporized carbon; and impinging the concentrated sunlight from the secondary concentrator onto the graphite to vaporize the graphite into a soot containing high amounts of fullerenes.

2. Description of the Prior Art

A short while ago, carbon was considered to exist in a limited number of forms such as diamond, graphite, glassy carbon, amorphous carbon, and a number of high-temperature species that existed in the vapor phase above 2,000° C. However, in 1984, mass spectrometry experiments revealed that carbon could possibly exist in a number of other forms ranging from C_{30} to C_{190}.

Approximately one year subsequent to 1984, the unique stability of molecular allotropic forms such as C_{60} and C_{70} was demonstrated ([H. W. Kroto et al; Nature 318, 162 (1985)]). These events led to the discovery of a whole new set of carbon-based substances known as fullerenes. Fullerenes are composed of closed polyhedra or tubes produced by carbon atoms linking together to form hexagons and pentagons as shown in FIG. 1.

The configuration of carbon atoms in fullerenes provides properties that have captured the interest of chemists, physicists, materials scientists, and medical researchers, as fullerenes have been shown to crystallize to form interesting solids and to polymerize in several ways to form new polymers. Also, metal atoms can be placed inside the fullerene cage to form encapsulated systems (i.e. UC_{28}, LaC_{82}, etc.), or outside the cage to form catalysts.

The fullerene cage can be reacted with other substances in a number of ways to form new molecules of interest.

Tubules of fullerenes have caught increasing interest as fibers, nanowires, and encapsulants. Fullerenes may also be doped to form electronic materials or reacted to form superconductors.

All of these applications have been discovered since the first macroscopic amounts of the most common fullerene, C_{60}, were isolated in 1990 [Kratschmer, et al., Nature 347, 354 (1990)].

Much of the work on fullerenes was performed using small amounts of material since synthetic approaches to these forms of carbon yielded limited quantities of material. The major drawback to the commercialization of some of the applications mentioned is due to the lack of a large-scaled method for producing and isolating fullerenes.

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Synthetic production of fullerenes was first provided using vaporization of graphite in an expanding helium atmosphere [H. W. Kroto, et al., Nature 318, 162 (1985)]. In this method, a Q-switched Nd: YAG laser is focused onto a rotating disc of graphite, whereupon carbon is evaporated or ablated into a high density helium flow. Clusters of soot form and are detected using a time-of-flight mass spectrometer. However, this method of production is sufficient to form only a few micrograms of fullerenes per day, which is only enough for certain limited research purposes.

A more useful method of synthesizing fullerene containing soot is the contact-arc method [Kratschmer, et al., Nature 347, 354 (1990)]. In this method, lightly contacting graphite electrodes are heated electrically by an alternating-current arc welder in an atmosphere of helium at a pressure of about 100 to about 200 torr. the graphite heats to evaporation at the contact and produces soot containing fullerenes. The soot condenses upon cool walls of a chamber, and is scraped off after a run that consumes the electrodes. Fullerenes are extracted from the soot by a solvent, such as toluene or benzene. This method is capable of producing a few tens of milligrams of fullerenes per run. While the apparatus used can be run in parallel so that the process is capable of producing several grams of fullerenes per day, the process is encumbered by scaling problems. For example, as the diameter of the rods are increased and the current supplied to the rods is increased to increase the amount of graphite evaporated per unit time, the yield of fullerenes decreases. ←

Rods that are ⅛" in diameter are capable of producing maximum yields of about 30%, while rods that are ¼" in diameter are capable of producing yields of around 15%, and rods that are ½" in diameter only have yields that are no more than 7%. The linear decrease in yield with an increase in rod diameter is not understood, but a reasonable conjecture put forth by Chibante, et al. [(J. Phys. Chem. 97(34), 8696 (1993)], is that the intense ultraviolet light in the plasma region of the arc may destroy fullerenes before they can exit that region. ←

Howard, et al. in Nature 352,139 (1991) discloses a third method of producing fullerenes. This method entails burning hydrocarbon feeds in an oxygen deficient flame or sooty flame. Benzene is used as a hydrocarbon source, with an argon diluted oxygen supply. In this method, it was found that soot yields are 0.2 to 12% of the carbon feed, and this gives a maximum yield of fullerenes of 0.3% of the carbon feed. This synthesis process is too costly to compete with the contact-arc process.

U.S. Pat. No. 4,874,596 discloses a method of changing the structure of a solid material in the form of carbon by converting the carbon to one or more other forms including diamond by the intense heat and shock wave force generated and transmitted through the material by intense radiation. This process does not provide caged molecular forms (fullerenes) nor does it encroach upon the physical concepts required for their production.

The three prior art methods of producing fullerenes, namely, laser ablation of graphite targets, the carbon arc process (also called the contact-arc process) and the process whereby soot produced by an oxygen deficient flame is utilized are encumbered by: the small capability of producing only milligram quantities of fullerenes at most; loss of efficiency as the electrode diameter is increased; and the high expense-low yields of soot from benzene (about 0.5%) that result in C_{60} costs of at least about $100.00/g.

Accordingly, there is a need extant in the art of producing fullerenes to provide a method for producing fullerenes that

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is greater than the milligram quantities presently available through current technology, by providing higher percentages of soot containing higher percentages of fullerenes, at lower cost.

SUMMARY OF THE INVENTION

Accordingly, one object of the invention is to provide a method for producing fullerenes in quantities greater than the few milligrams of fullerenes produced per day by the laser ablation of graphite technique method.

A further object of the invention is to provide a method for producing fullerenes in greater quantities than the gram quantities of material produced per day per unit, without encountering loss of efficiency in production with increases in the electrode diameters using the carbon-arc process (also called the contact-arc process).

A yet further object of the invention is provide a method for producing fullerenes in which the amount of soot is greater in quantity than that which is produced by the oxygen deficient flame process, so that the amount of soot and the quantity of fullerenes contained therein is produced in greater yield.

A still further object of the invention is to provide a method for producing higher yields of fullerenes having a particular molecular weight in soot.

In general, the process of the invention is accomplished by delivering highly concentrated solar radiation onto a graphite target from a focal point of a solar furnace by: providing a solar furnace having a primary concentrator with a focal point that concentrates a solar beam; providing a reflective secondary concentrator having an entrance aperture and an exit aperture at the focal point of the solar furnace; providing graphite at the exit aperture of the secondary concentrator; flowing argon gas over the graphite to keep the secondary concentrator clean of vaporized carbon; and impinging the concentrated sunlight from the secondary concentrator onto the graphite to vaporize the graphite into fullerenes containing soot.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 shows spherically shaped fullerene molecules containing from C_{28} to C_{540} atoms, located at vertices.

FIG. 2 shows the high-flux solar furnace in which a heliostat (A) tracks the sun and directs the sunlight into a bank of concentrating mirrors (B), after which a concentrator array focuses the sunlight to a focal plane (target plane) inside a bay area (C), that houses the target, control room, and control functions of the furnace.

FIG. 3 shows the apparatus in which the graphite pellet is placed in proximity to the secondary concentrator.

FIG. 4 shows flux measurements, wherein the measured peak flux is plotted as a function of attenuator opening that makes flux in a given concentration available at the exit of the secondary concentrator.

FIG. 5 shows flux measurements plotted as a function of different distances from the secondary concentrator exit with different numbers of concentrator facets uncovered.

FIG. 6 shows a graph of a mass spectrum of C_{60} in soot produced at the solar furnace, where a 1-mg sample of soot was heated to 600° C. in flowing helium (5 L/min.) at the entrance orifice of a molecular beam mass spectrometer.

FIG. 7 is a graph showing High Pressure Liquid Chromatography (HPLC) of the toluene soluble extract from soot produced in the solar furnace using the process of the invention.

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DETAILED DESCRIPTION OF THE INVENTION

All fullerene production methods require a source of small, gas phase carbon clusters (1 to possibly 10 atoms). Two sources of these clusters exist. One method is the combustion of hydrocarbons such as benzene in an oxygen deficient flame to produce a soot along with other combustion products such as H_2O, CO, and CO_2.

While the percentage of fullerenes in the soot may be relatively high, the yield of fullerenes compared to mass of hydrocarbon consumed is low.

The second general method for production of fullerenes uses an energy source to vaporize elemental carbon at temperatures above 3000° C., whereupon the vaporized carbon then condenses into carbon soot. The number of energy sources utilized to vaporize the carbon include lasers, plasmas, induction heating, and arcs struck between graphite rods.

While the arc method has proven to be the most useful, even this method yields only ten's of grams of fullerenes per hour, and none of the existing methods have been brought to large-scale production.

Fullerenes are spherically or tubularly shaped molecules of carbon consisting of from 28 to more than 240 carbon atoms. They are sometimes called "Buckeyballs", "Buckeytubes", or "Buckminister fullerenes" to describe the cage-like structures of the molecules. The typical "Buckeyball" is the C_{60} molecule, which is a truncated icosohedron typified by the soccer ball, with carbon atoms at the 60 vertices of the pentagons and hexagons that form a nearly spherical surface.

Spherical shaped fullerene molecules containing from 28 to 540 carbon atoms are shown in FIG. 1.

Alternately, tubules (sometimes called nanotubes) can be formed where single (or multiple layers) of graphitically bonded (sp^2) sheets are rolled to form a tube, which is capped by a hemispherical fullerene molecule.

Tubules can have diameters as small as 1 nm and they may have aspect ratios (l/d) as large as 10^4 to 10^5. The calculated tensile strengths of such fibers is enormous.

The system for providing fullerenes of the invention process utilizes highly concentrated sunlight delivered to graphite targets, so that the graphite evaporates and produces fullerenes. The heating process occurs solely from the application of radiant energy from the sun, and no other conversion processes are required. Further, no other energy resources are required, and fullerenes are produced in an energy efficient method without the environmental liabilities associated with fossil or nuclear energy.

The primary apparatus used is a high flux solar furnace at South Table Mountain in Golden, Colo. FIG. 2 is a photograph inclusive of a cut-away of the facility showing a heliostat (A) that tracks the sun and directs the sunlight into a bank of concentrating mirrors (B). The concentrator array focuses the sunlight to a focal plane (target plane) inside of the experimental bay area (C) that houses the target, control room, and all control functions for the furnace. Vacuum chambers, pumps, and a gas supply system are used inside of the bay room to control the processing environment.

The environmentally controlled target chamber consists of a target zone enclosed with a silica or quartz window to admit the sun, a gas supply system, and a vacuum system that allows very clean environments to be maintained. Base pressure in the vacuum system is 10^{-8} torr, and it is equipped with a residual gas analyzer (RGA).

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In order to provide fullerenes in accordance with the invention, a process chamber was designed to incorporate a secondary concentrator to boost the flux to useful levels for evaporating graphite. A schematic of this chamber is shown in FIG. 3, where solar radiation from the primary concentrator passes through a quartz window 4 and through a secondary concentrator 5 having an entrance aperture and an exit aperture at the focal point of the solar furnace. A graphite target 6, placed on a target support 7 at the exit aperture of the secondary concentrator, is vaporized to fullerene containing soot by impinging concentrated sunlight. The apparatus which produces the soot containing fullerene is equipped with a gas inlet 8 stacked on top of and in close proximity to the secondary concentrator. Argon gas is passed through the inlet port and through the secondary concentrator in a manner so that it impinges on the graphite sample and is then removed by a vacuum pump (not shown) through vacuum port 9. A capacitance manometer 10 is used to measure the gas pressure during the process.

It is important to note that the solar beam is admitted through a high purity fused silica window from the primary concentrator bank. Thereafter, the secondary concentrator concentrates the light down so that the flux is increased by about a factor of 10. The highly concentrated solar beam then impinges upon a graphite target, which may be a rod, button or shaped target or a receptacle containing graphite powder. A tantalum shield 11 deflects radiation from the target and prevents overheating of the stainless steel chamber.

Flux measurements were conducted to ensure that the graphite sample temperature was in the range of vaporization. The results of the flux measurements are shown in FIGS. 4 and 5, where the data in these figures were normalized to a direct-normal irradiance of 950 W/m², which was representative for the days the tests were conducted.

In FIG. 4, the measured peak flux is plotted as a function of the attenuator opening. With the attenuator fully opened, a flux of over 1,300 W/cm² (corresponding to a 13,000 concentration just under 15,000) was available at the exit of the secondary concentrator. The data in FIG. 4 was measured with all 25 of the primary concentrator facets uncovered. Similarly, all of the facets were uncovered in the production of fullerenes.

The flux is plotted as a function of different distances from the secondary concentrator exit in FIG. 5. These measurements were compared to the flux predicted by a Monte Carlo computer code, SOLFUR, written to explicitly model the various optical components of solar furnaces. By using an additional code specific to reflective secondary concentrators, the set of rays from SOLFUR was traced from the entrance plane of the secondary concentrator to a plane placed at various distances below the exit. The data measured in FIG. 5 was gathered with 19 of the primary concentrator facets uncovered.

The reaction chamber of the apparatus used to produce fullerenes in the invention process is disposed vertically, and is a vacuum sealed system with gas flow ports that permit the fullerene production to be conducted in an oxygen and water free environment. It is sealed on top with a quartz window using a Viton O-ring.

The gas inlet port and the secondary concentrator are disposed beneath the quartz window, and a needle valve outside of the reaction chamber regulates gas flow into the chamber.

The carbon sample sits at the exit aperture of the secondary concentrator, which is in the region of highest solar flux.

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The secondary concentrator and the horizontal surface just beneath it have internal cooling channels that are connected to cooling lines.

The bottom section of the reaction chamber is connected to a pumping system fitted with a mechanical pump, a turbo molecular pump, a butterfly valve, and a residual gas analyzer (RGA).

When the concentrated solar flux (approximately 1300 W/cm²) impinges on the top surface of the graphite or carbon sample, the sample vaporizes and carbon vapor condenses in a dry ice trap and on the chamber walls as soot.

Throughout the run, an inert gas (argon) was passed from the inlet port, through the secondary concentrator, over the carbon sample, and then out of the vessel through the vacuum pumping port. In addition to providing an oxygen-free environment, the flowing gas helps to cool the system and keeps the secondary concentrator clean by sweeping the carbon vapor away from its reflective surface.

Graphite was used as the carbon source and the samples were cut from a 0.75-cm thick slab of 99.999% purity graphite. Several 1-cm-diameter cylinders were cut from this slab. Unmodified and modified graphite cylinders were used in the runs. Modified graphite samples were modified by bevelling the top edge to form a conical shape or by cutting a small, hemispherical cavity into the top surface.

For each run, a graphite sample was placed at the exit of the secondary concentrator and the secondary concentrator was at the High Flux Solar Furnace's (HSFS's) focal point. After connecting the chamber to the vacuum system and the cooling lines, the reaction chamber was subjected to a pumping and purging process to clear it of air and water vapor. The chamber was then pumped down to 50 mtorr, and backfilled with argon to 400 torr. This pumping followed by purging was repeated four times, after which the argon inlet valve was closed, and the vessel was pumped down to 5×10⁻⁵ torr to ensure that it was not leaking.

The argon flow was adjusted to the proper level and the butterfly-valve setting was adjusted to bring the chamber to the desired pressure (either 50 torr or 100 torr). Once the chamber pressure was steady, the chamber was illuminated with the attenuated concentrated solar beam for approximately three minutes to "bake out" any impurities in or on the graphite sample. After this baking-out period, the sample was removed from the chamber, weighed, and replaced.

The above procedures were repeated beginning with pumping and purging and finishing with the chamber pressure adjusting. The graphite sample was then exposed to the concentrated beam for a period of from about 30 seconds to about two minutes. After exposure to the flux, the reaction chamber was opened and the soot was removed from the condensing surfaces with a small brush, bottled, and the graphite sample was reweighed.

As shown in the graph of FIG. 6, a mass spectrum of C₆₀ in soot was produced at the solar furnace, where a 1-mg sample of soot was heated to 600° C. in flowing helium (5 liters/minute) at the entrance orifice of a molecular beam mass spectrometer. In this graph, the vertical axis shows relative intensity and the horizontal axis shows the mass. The mass spectrum shows significant peaks at 360 amu and 720 amu for the doubly and singly charged C₆₀ molecules.

There were several variables in the operating conditions that had the potential of affecting the optimization of fullerene yield. To determine the influence of the different variables, a Plackett-Burman design of balanced incomplete blocks was used to design a set of runs.

The Plackett-Burman design is a two-level method ("plus" denoting high level and "minus" low level) of

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experimental design where as few as N experiments can be used to study the effect of as many as N-1 variables (Stowe et al., "Efficient Screenings of Process Variables", Industrial and Engineering Chemistry, 1966, pp. 36-40).

The variables are usually associated with an experimental parameter (i.e., gas pressure), but they can be dummy variables. Dummy variables are not associated with any experimental parameters, but instead add more experiments to the design and thereby refine the statistical calculations of variable effect and standard error.

According to the Plackett-Burman design, the effect of any one variable on the experimental result is determined by the difference between the average value of the results for the positive runs less the average value of the results for the negative runs, as per Equation 1.

$$E_{variable} = \frac{\Sigma R_{(+)}}{No.\ of\ (+)\ runs} - \frac{\Sigma R_{(-)}}{No.\ of\ (-)\ runs} \qquad Eqn.\ (1)$$

where,

$E_{variable}$=effect of variable on results (% fullerene yield),

$R_{(+)}$=results from experiments with variable at positive value,

$R_{(-)}$=results from experiments with variables at negative value.

The standard error in the effect is calculated with Equation 2.

$$SE_{effect} = \sqrt{\frac{\Sigma (E_{dummy})^2}{n}} \qquad Eqn.\ (2)$$

where,

SE_{effect}=standard error of any effect calculate with Equation 2,

E_{dummy}=effect of dummy variable(s) on result,

o=number of dummy variables.

In the operating runs, the effects of seven different variables were considered. According to the Plackett-Burman method, this required a set of eight runs. The variables and their high-and-low values are given in Table 1. Table 2 has the distribution of the high and low parameters throughout the set of eight runs.

TABLE 1

Variables and parameters used for the Plackett-Burman design

Variable	High Parameter (+)	Low Parameter (-)
A = Solar flux	1300 W/cm²	1150 W/cm2
B = Position of sample	at secondary concentrator exit cavity	2 mm below concentrator exit cone
C = Sample shape	cavity	cone
D = Length of exposure	2 min	1 min
E = Gas flow rate	4 slm	2 slm
F = Type of gas	He	Ar
G = Gas pressure	100 torr	50 torr

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TABLE 2

Plackett-Burman matrix for parameters.

Run	A	B	C	D	E	F	G
1	+	+	+	-	+	-	-
2	+	+	-	+	-	-	+
3	+	-	+	-	-	+	+
4	-	+	-	-	+	+	+
5	+	-	-	+	+	+	-
6	-	-	+	+	+	-	+
7	-	+	+	+	-	+	-
8	-	-	-	-	-	-	-

A series of preliminary runs were made to determine the high-low limits given in Table 1. For example, in one set of runs, it was observed that very little soot was produced for exposure times less than one m¹ tae. As the exposure time was lengthened beyond one minute, it was observed that the temperature of the apparatus became dangerously high after approximately two minutes. Therefore, the type of gas was kept constant throughout the set of eight runs and the variance "F" became a dummy variable. It appeared that the superior heat transfer characteristics of helium, as compared to argon, prevented the carbon sample from reaching a high enough temperature for vaporization.

Again, during the preliminary runs, mass spectrometry was used to confirm the existence of C_{60} in the collected soot, and FIG. 6 shows the mass spectrum of a 1 mg soot sample produced during preliminary runs.

The set of eight runs were performed under the conditions prescribed in Table 2.

Table 3 gives the mass of soot produced during each of the runs and the percentage of C_{60} in each soot sample.

TABLE 3

Masses of soot produced during two level experiments and corresponding fullerene yield.

Run	Soot Mass (mg)	% Yield of Fullerenes
1	7.0	3.2
2	7.6	12.8
3	7.0	3.2
3	0	NA
4	4.7	7.3
5	0	NA
6	0	NA
7	12.6	13.9
8	0	NA

In Table 3, it is shown that only half of the runs resulted in appreciable soot production. Examination of the data reveals that all of the runs with the sample at the concentrator exit resulted in a measurable amount of soot, but no soot was produced in the runs where the sample was about 2 mm or more below the concentrator exit. Therefore, the graphite sample should be 2 mm or less below the secondary concentrator exit. This is an indication that the negative value for the sample positioning was too extreme.

Of the soot-producing runs, run 7 showed the most promising results, as this run resulted in the largest amount of soot and the highest yield. Although the difference in the percent yield between runs 7 and 2 appears to be within the margin of experimental error (13.9% vs. 12.8%), the difference in the amount of fullerenes produced is significant. Run 7 resulted in approximately 1.8 mg of fullerenes compared to just under 1 mg in run 2. Run 2 and run 7 were both

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performed with a high exposure length and a low gas flow rate, but run 7 was performed with a low flux parameter, a cavity-shaped sample, and a low chamber pressure.

During these runs, it was apparent that the cavity-shaped samples often showed much greater signs of vaporization activity than the conical-shaped samples. Sample shape is therefore the likely parameter responsible for the large amounts of soot (and hence greater fullerene production) in run 7.

FIG. 7 shows the retention-time plot from the HPLC analysis of soot run 7.

The effects of the different experimental variables and the associated standard error were calculated using Equations 1 and 2. These statistical results are given in Table 4.

TABLE 4

Relative effects of experimental variables and the standard error on percent fullerene yields.

Variables	Effect
Position of sample (B)	9.3
Length of exposure (D)	4.05
Gas flow rate (E)	4.05
Solar flux (A)	1.3
Dummy (F)	1.3
Sample shape (C)	0.75
Chamber pressure (G)	0.75
Standard Error	1.3

The relatively large standard error in the effect calculations eliminates the significance of the effects calculated for three of the variables: the solar flux (A); the shape of the sample (C); and the chamber pressure (G). However, the calculated effects of the remaining three variables are outside of the standard error range.

It is apparent that the position of the sample relative to the secondary concentrator exit had the most significant effect.

The effects of the length of exposure and the gas flow rate calculated to be the same. The fact that no soot was ever produced when the carbon sample was in its low position increased the likelihood for two effects to calculate the same value. The fact that the four runs with low sample position resulted in no soot production lessened the impacts of these runs. The effects of the length of exposure and the gas flow rate were probably not equally significant to the fullerene yield.

It was noted that the effect of the rate of gas flow was actually a negative value; in other words, a low gas flow rate was more conductive to fullerene production.

It appears that the high gas flow cooled the graphite sample, and thereby inhibited vaporization.

Although the low sample position was too extreme to realize the full benefit of the Plackett-Burman design, the effect analysis was still beneficial. The calculated effects revealed that the carbon sample should be positioned at the concentrator exit, and that the lower gas flow rate and the longer exposure times were both conducive to high yields of fullerenes.

Percent yields for the soot samples were determined by toluene extractions from run 7 and matching their high-pressure liquid chromatography (HPLC) retention times with toluene extracts from commercially available soot samples. The yield analysis was performed on a Hewlett Packard Model 1050 HPLC instrument using a reverse phase column (HP 5μ silica, 300 Å pore size) with toluene/methanol (45:55 at 2 mL/min) as the eluant, and the results are shown in FIG. 7.

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While the preferred method of producing soot containing high amounts of fullerenes will utilize a solar furnace having a primary concentrator, followed by the use of a secondary concentrator having an entrance aperture and an exit aperture at the focal point of the solar furnace so as to affect impingement of a concentrated beam of sunlight from the secondary concentrator onto the carbon source to vaporize the carbon source into soot containing high amounts of fullerenes, it is to be understood that the use of a primary concentrator alone will suffice to provide producing soot containing high amounts of fullerenes if the concentrated beam of sunlight is sufficient to cause evaporation of carbon and subsequent formation of fullerenes. In the context of the invention, it has been found that, when a primary concentrator is focused to provide a concentrated solar beam having a flux of between about 250 W/cm^2 to about 2,000 W/cm^2, the carbon source will vaporize into a soot containing high amounts of fullerenes.

As a result of the invention process, larger amounts of fullerenes can be economically prepared from soot obtained using concentrated solar flux as a supply of source material. The present invention therefore provides a highly economical and useful process for producing fullerenes.

While fullerenes of clusters of carbon atoms ranging from $C_{28}-C_{540}$ range were produced, only small amounts of fullerenes having carbon atoms greater than the C_{60} and C_{70} (the most common forms of fullerenes) were produced.

In selecting the carbon source material for production of fullerenes in accordance with the invention process, diamond, graphite, graphite powder, glassy carbon, amorphous carbon, hydrocarbon feed and benzene will suffice; however, graphite is preferred. Graphite having a hemispherical cavity in its top surface is most preferred, as it provides greater amounts of soot containing higher amounts of fullerenes.

Any of the inert gases will suffice in the context of the invention for purposes of keeping the secondary concentrator free from vaporized carbon; however, argon is preferred as it has less of a tendency to prevent vaporization of the soot produced in the solar furnace.

The foregoing description is illustrative only of the principals of the invention. Further, since numerous modifications and changes will readily occur to those skilled in the art, it is not desired to limit the invention to the exact construction and operation shown and described, and accordingly, all suitable modifications and equivalence may be resorted to within the scope of the invention as defined by the claims which follow.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows.

What is claimed is:

1. A method of producing soot containing fullerenes solely from the application of radiant energy from the sun to a carbon source material comprising:

providing a solar furnace having a primary concentrator with a focal point that concentrates a solar beam of sunlight;

providing a reflective secondary concentrator having an entrance aperture and an exit aperture at the focal point of the solar furnace;

providing a carbon source material less than about 2 mm below the exit aperture of the secondary concentrator;

supplying an inert gas over the carbon source material to keep the secondary concentrator free from vaporized carbon; and

impinging a concentrated beam of sunlight from the secondary concentrator onto the carbon source material

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less than about 2 mm below said exit aperture to vaporize the carbon source material into a soot containing fullerenes.

2. The method of claim 1, wherein the concentrated solar flux is between about 250 W/cm^2 to about 2,000 W/cm^2.

3. The method of claim 1, wherein the fullerenes in the soot are selected from the group consisting of clusters of carbon atoms in the C_{28}-C_{540} range.

4. The method of claim 3, wherein the fullerenes in the soot are selected from a group consisting of clusters of carbon atoms in the C_{60}-C_{70} range.

5. The method of claim 3, wherein the solar furnace is vacuum-sealed and has a top section which includes a quartz window.

6. The process of claim 5, wherein the carbon source is selected from the group consisting of: diamond, graphite, amorphous carbon, and hydrocarbon feed.

7. The process of claim 6, wherein the carbon source is graphite.

8. The process of claim 7, wherein the inert gas is selected from the group consisting of helium and argon.

9. The process of claim 8, wherein the inert gas is argon.

10. The process of claim 9, wherein the concentrated solar flux from the primary concentrator has a 12 cm diameter and a peak flux of about 250 W/cm^2.

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11. The process of claim 10, wherein the secondary concentrator has a concentrated solar flux range of between about 1300 W/cm^2 and about 2000 W/cm^2.

12. The process of claim 11, wherein the graphite is in the form of a cylinder.

13. The process of claim 12, wherein the graphite is in a conically shaped form.

14. The process of claim 11, wherein the graphite has a hemispherical cavity in a top surface thereof.

15. The process of claim 11, wherein the graphite is exposed to the concentrated beam from the secondary concentrator for a period of from about 30 seconds to about 2 minutes.

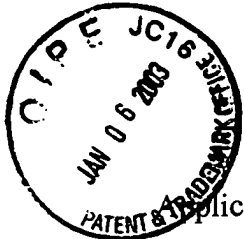16. The process of claim 15, wherein the fullerene is a C_{60} fullerene.

17. The process of claim 15, wherein the fullerene is a C_{70} fullerene.

18. The process of claim 15, wherein the fullerene is a C_{76} fullerene.

19. The process of claim 15, wherein the fullerene is a C_{78} fullerene.

20. The process of claim 15, wherein the fullerene is a C_{84} fullerene.

* * * * *

Applicants: Donald R. Huffman, et al.

Serial No.   08/471,890

Docket: 7913ZY

Filing Date: June 7, 1995

Examiner: S. Hendrickson

Group Art Unit: 1754

Title: SUPPLEMENTAL DECLARATION OF HAROLD W. KROTO UNDER 37
                C.F.R. §1.132

PATENTS

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s): Donald R. Huffman et al.   Examiner: P. DiMauro

Serial No.: 08/236,933

Art Unit: 1103

Filed: May 2, 1994

Docket: 7913zazy

For: NEW FORM OF CARBON

Assistant Commissioner for Patents
Washington, DC 20231

SUPPLEMENTAL DECLARATION OF HAROLD W. KROTO UNDER 37 C.F.R. §1.132

I, HAROLD W. KROTO, PH.D., declare and say as follows:

1.   I am the Royal Society Research Professor in the School of Chemistry and Molecular Sciences at the University of Sussex, Brighton, United Kingdom (one of only twenty such appointments in the United Kingdom). In addition, I have been awarded over one dozen honorary degrees from various universities. In 1996, I, along with Robert Curl and Richard Smalley, received the Nobel Prize in Chemistry for our discovery of fullerenes. Earlier that year, I was also awarded Knighthood for my contributions to chemistry. For the convenience of the United States Patent and Trademark Office, I have attached hereto as Exhibit 1 my curriculum vitae, which describes my credentials and demonstrates my expertise in the area of fullerenes.

2.   I am intimately familiar with the literature concerning and was personally involved in the search for C_{60} and other fullerenes. I have written several articles on the

subject, as evidenced by the publications listed in Exhibit 1, including the first definitive and only complete review on the subject in Kroto, et al., in <u>Chemical Review 1991</u>, 91, 1213 - 1235. I therefore believe that it is fair to say that I am among the recognized experts on the subject of fullerenes.

3.   This Declaration supplements and is not intended to replace the previous Declarations which were executed on July 27, 1995 and June 9, 1995, the contents of which are incorporated herein by reference.

4.   I have been requested by applicants' attorney to read and review the above-identified application, i.e., USSN 08/236,933 and the pending claims therein. In addition, I have been requested by applicants' attorney to comment on my understanding of the terms "macroscopic amounts" as applied to fullerenes, including C_{60}, in the claims and to comment on whether, in my opinion, the underlying specification clearly describes a process for making fullerenes, including C_{60}, in macroscopic amounts without an undue amount of experimentation.

5.   As requested, I have read and reviewed the above-identified application, including the pending claims in the above-identified application. It is my understanding that the claims in the above identified application are directed, among other things, to a process of producing C_{60} in macroscopic amounts.

6.   I have been advised that there is a companion application, USSN 486,669, on file in the United States Patent

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and Trademark Office. I have been advised that, except for the claims, the disclosure in the '669 application is identical to that of the above-identified application. I have also reviewed the pending claims related thereto. It is my understanding that these claims are directed, among other things, to a process for making fullerenes in macroscopic amounts.

7. I have also been advised of the existence of two more applications, namely USSN 580,246 and USSN 471,890. It is my understanding that the former application is directed to, among other things, C_{60} in macroscopic amounts, while the latter is directed to, among other things, fullerenes in macroscopic amounts. It is also my understanding that, except for the claims, the respective specifications are not only identical, but also are identical to the specification of the above-identified application.

8. It is my opinion that the above-identified specification describes the preparation of fullerenes, including, for example, C_{60}, in macroscopic amounts. This is based upon my understanding of the application and my repetition of the procedure described in the underlying application for producing fullerenes, including C_{60}, and isolation thereof in macroscopic amounts.

9. It is my opinion that the term "macroscopic amounts" as used in the claims is clearly understood by the ordinary skilled artisan. It is my understanding that the term is being used in its plain and ordinary meaning to connote that

-3-

the process described in the underlying specification produces
fullerenes, including, for example, C_{60}, in amounts which can
be seen easily with the naked eye. This is consistent with the
definitions of "macroscopic", as defined in the McGraw Hill
Dictionary of Scientific and Technical Terms, 4th ed., p.1125,
1989, where it is defined as "large enough to be observed by
the naked eye," and in Hackh's Chemical Dictionary, 4th ed.,
wherein it defines macroscopic as describing "objects visible
to the naked eye."

    10. "Fullerenes", in my opinion, is a term of art
that is also widely understood by the scientific community; it
was adopted to conveniently describe the family of caged carbon
molecules represented by C_{60}. See, e.g., the section entitled
"Fullerene" in the Concise Encyclopedia of Science and
Technology, 3rd ed., Sybil P. Parker, ed., McGraw Hill, NY, NY,
p. 819 (1994), attached hereto as Exhibit 2. This section,
which was written by me, describes fullerenes as an even number
of carbon atoms arranged in a closed hollow cage, and
specifically exemplifies fullerene-60, or C_{60}, as a species of
fullerenes. However, there are other species of fullerenes,
and many of those can and have been prepared by the process
described in the above-identified specification.

    11. The above-identified application describes in
great detail the process for producing fullerenes, including
C_{60}. As an example thereof, attention is directed to Example 1
on Page 16 of the above-identified application which describes

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a process for making fullerenes, including C_{60}, by (1)
vaporizing graphite rods in a conventional bell jar evaporator
in the presence of an inert quenching gas, e.g., helium or
argon, to produce carbon smoke; (2) collecting the smoke
formed; (3) then extracting the fullerenes, including C_{60},
using benzene, or other inert solvent; (4) then, after
evaporating the solvent, subliming the impure product; and (5)
then collecting the sublimed product.

12.   The specification on Pages 3-8 describes a more
general process for preparing fullerenes, including C_{60}, and
describes other means for extracting fullerenes, including C_{60},
from the smoky carbon product, including sublimation and the
use of other non-polar solvents to extract the fullerenes,
including C_{60}, from the smoky carbon product.

13.   It is my opinion that a person of ordinary skill
in the art in 1990 reading the specification would understand
the specification to be directed to the class of carbon
structures that have come to be commonly referred to as
fullerenes.   There is no question that the specification
describes, among other things, C_{60} and C_{70}, which are designated
as fullerene-60 and fullerene-70, respectively.   These are
species of fullerenes, and the skilled artisan would comprehend
that the specification is directed to fullerenes.   Moreover,
spectral data, especially mass spectra data of the smoky carbon
product produced from the vaporization of the elemental carbon
in the inert quenching gas, in accordance with the procedure

-5-

described in the above-identified application, reveals that the
smoky carbon product contains other species of fullerenes;
although not in the abundance of fullerene-60 or fullerene-70
nevertheless, collectively in macroscopic amounts in the soot.
Moreover, at the time of September 1990, various other hollow
caged species containing solely carbon atoms, now known as
fullerenes, had been postulated. So even if not specifically
mentioned in the application, these other species of fullerenes
were inherently present in the carbon soot produced by the
process described in the underlying application -- a fact
verified by experimentation. Consequently, it is my opinion
that the ordinary skilled artisan in 1990 would understand that
the above-identified specification is directed to, among other
things, a process for making fullerenes, including C_{60}.

14. Moreover, it is my opinion that the ordinary
skilled artisan in September 1990 reading the specification
would understand that the teachings therein were applicable for
preparing and isolating not only C_{60} and C_{70}, but also other
fullerenes without an undue amount of experimentation. Thus,
the above-identified application paves the road for preparing
and isolating other fullerenes species without an undue amount
of experimentation.

15. Moreover, the specification provides evidence in
several instances that the inventors had produced the fullerene
products, including C_{60}, in macroscopic amounts. For example,
attention is directed to Example 1 which describes the product

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thereof in powder form as brownish-red. Such language
connotes, in my opinion, that the product thereof could be seen
with the naked eye. Moreover, based upon repetition of the
process described therein, as described hereinbelow, the
process as described in the above-identified application,
especially in Example 1, inherently produces fullerenes, e.g.,
C_{60}, in amounts that could be seen with the naked eye.

16. Moreover, these concepts discussed in Paragraphs
13-15 are clearly corroborated when the ordinary skilled
artisan repeats the procedures described in the above-
identified specification for preparing the fullerenes.

17. Utilizing the procedure exactly as described in
the above-identified application, I have had fullerenes,
including C_{60}, prepared in macroscopic amounts on numerous
occasions since 1990 to the present. More specifically, by
following the procedure described in the above-identified
application and vaporizing graphite rods in an atmosphere of
helium, forming the carbon soot therefrom, collecting the soot
and dissolving the soot in benzene, in accordance with the
procedure described in the above-identified application, I and
my colleagues have prepared and identified various fullerenes,
including, inter alia, C_{60}, C_{70}, C_{76}, C_{78}, C_{6}, C_{94} and C_{86}.

18. Moreover, by following the procedure described
in the above-identified application, and in accordance with the
procedure outlined in Paragraph 17 herein, I have isolated
fullerenes in macroscopic amounts, as defined herein. For

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example, utilizing the procedure outlined in Paragraph 17, I
have found that the smoky carbon product contains 5 to 10% C_{60}
and 1% C_{70}. We routinely produce the soot in 1-5 gram
quantities and routinely extract 100-500 milligram amounts
batchwise. Thus, one kilogram of sooty carbon product
produces, on average, 100g of C_{60}, 10g of C_{70} and 1 gram of
other fullerenes, such as those indicated hereinabove. The
various fullerenes formed can and are isolated in accordance
with the isolation and purification procedures described in the
above-identified application, without an undue amount of
experimentation. Furthermore, the various fullerenes are
isolated as solids, which are easily visible to the naked eye.
For example, in a typical experiment conducted according to the
procedure described in the above-identified application, C_{60} is
formed in about 100 mg quantities C_{70} in about 10 mg quantities
and the remainder in about 1 mg quantities.

19. Thus, by following the procedure described in
the above-identified application, I have found that the process
described therein inherently produces several species of
fullerenes, including C_{60}, in macroscopic amounts. In fact, by
following the procedure of Kratschmer and Huffman, outlined in
the above identified application, crystalline material of
fullerenes, including C_{60}, is produced which can be seen with
the naked eye.

20. Moreover, there is additional evidence to
support the statements made in Paragraph 19.

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21. Attention is directed to an article by Kratschmer, et al. in Nature, 347, No. 6391, pp. 354-358 (1990), attached hereto as Exhibit 3. It was the first publication that describes the preparation and isolation of macroscopic amounts of a compound, e.g., C_{60} and C_{70}, having the fullerene structure.

22. It is interesting to note there are over 3,390 publications referring to their Nature article. Only a handful of papers in some fifty years of science receive this number of citations. It is apparent that the Nature article has been cited an innumerable number of times because various scientists have followed the procedures described therein to successfully produce macroscopic quantities of fullerenes, including C_{60}. The fact that several thousand publications reference the Nature article for preparing fullerenes adds further support that the procedure described in the Nature article and thus the present specification provides sufficient information for the skilled artisan to generally make macroscopic amounts of fullerene, including C_{60}, without an undue amount of experimentation. Moreover, it is also attributable to the due recognition by the scientific community of Kratschmer's and Huffman's claim to have originated this method of production.

23. The realization by Huffman and Kratschmer of macroscopic quantities of fullerene and the isolation and characterization of C_{60} and C_{70} by the methods described in the above-identified application is recognized by the knowledgeable

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scientific community as a long awaited and much needed breakthrough; it was surprising that relatively high yields of fullerene such as C_{60} could be achieved by these methods, as it was generally expected that infinitesimal amounts of fullerenes would exist in the soot product and that it would require very sophisticated equipment to isolate quantities of material required to establish and confirm the existence of the products. The difficulties that existed in the quest for C_{60} are well elaborated in the article entitled "Fullerenes" by Robert F. Curl and Richard E. Smalley, printed in Scientific American, Oct. 1991, pp. 54-62 attached hereto as Exhibit 4.

24. Although the discovery described in the Huffman and Kratschmer application may seem simplistic to the uninformed, especially in hindsight, their discovery was quite remarkable. The Kratschmer and Huffman method described in the above-identified application is all the more remarkable for the fact that so simple a procedure so readily produces large amounts of fullerenes. This is readily appreciated if one considers the historical perspective. Even since the detection of C_{60} by the collaborative efforts of the Smalley and Kroto groups in 1985, as described in the article in Nature, 1985, 318, 162-163, attached hereto as Exhibit 5, experts, such as Drs. Smalley and myself, both together and separately worked to prepare fullerenes on a larger scale. For five long years, many attempts were tried, but each was unsuccessful. Finally, to my expert knowledge, one group, Huffman and Kratschmer, was

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the first to find and publish a methodology capable of producing and isolating fullerenes, such as C_{60}, in macroscopic amounts. This methodology is described in their application and satisfied a long felt need in this area.

25. Furthermore, one should not underestimate the significance of their discovery. For the first time, scientists were able to produce and work with samples of fullerenes. They were able to confirm the theoretical prediction about fullerenes and continue to explore new properties of same. Their discovery spawned enormous scientific interest, as evidenced by the 3390 citations to the Nature article in Exhibit 3 for making fullerenes. As a consequence, innumerable investigations and studies relating to fullerenes were conducted, generating several thousand publications on the subject. In short, I cannot emphasize enough that their discovery revolutionized the area of fullerenes by making it possible for experimental researchers worldwide to study their chemical and physical properties.

26. The scientific community has unanimously and unequivocally acknowledged and recognized that Kratschmer and Huffman have developed a process for preparing fullerenes, e.g., C_{60}, in macroscopic amounts, and in consequence thereon has presented them with several awards. Even the press release by the Royal Swedish Academy of Sciences regarding the Nobel Prize in Chemistry in 1996, attached hereto as Exhibit 6, recognizes the contribution of Huffman and Kratschmer by

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acknowledging that they for the first time produced "isolable quantities of C_{60}". (See Page 2 of Exhibit 6). As stated in the press release:

> [t]hey obtained a mixture of C_{60} and C_{70} the structures of which could be determined...The way was thus open for studying the chemical properties of C_{60} and other carbon clusters such as C_{70}, C_{76}, C_{78} and C_{94}...An entirely new branch of chemistry developed with consequences in such diverse areas as astrochemistry, superconductivity and materials chemistry/physics...

27. Thus, in my opinion, there is no reasonable doubt that the above-identified application describes a process for preparing fullerenes, including C_{60}, in macroscopic amounts and the process described therein provides sufficient detail for an ordinary skilled artisan in 1990 to make the same without an undue amount of experimentation.

28. I have reviewed pages 2-4 of the Office Action issued in the above-identified application and in USSN 486,669. In the Office Action in the above-identified application, the Office Action equates tonnage quantities with the term "macroscopic". It is my opinion that such logic is unjustified, since the skilled artisan would not equate "macroscopic amounts" with tonnage quantity. As defined hereinabove, macroscopic amounts is that amount which can be seen by the naked eye. As explained hereinabove, by following the procedure described in the application, macroscopic amounts of fullerenes, including C_{60}, are obtained. In fact, gram quantities are routinely available by the Kratschmer and

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Huffman method described in the above-identified application,
which amounts are in macroscopic amounts in accordance with the
standard use of that term. Moreover, it is my opinion that the
embodiment in the above-identified application can be modified
without an undue amount of experimentation to produce
fullerenes, including C_{60}, in a continuous process.

29. In USSN 486,669, the Office Action alleges that
the application does not describe nor provide sufficient
information to permit one skilled in the art to easily produce
caged carbon molecules consisting solely of carbon atoms which
are soluble in non-polar organic solvents. I disagree
absolutely and totally. In my opinion, the term "caged carbon
molecules consisting solely of carbon atoms which are soluble
in non-polar organic solvents" uniquely describes fullerenes,
and as indicated hereinabove, it is my opinion that the
application describes the preparation of macroscopic amounts of
fullerenes.

30. I further declare that all statements made
herein of my own knowledge are true and that all statements
made on information and belief are believed to be true, and
further that these statements were made with the knowledge that
willful false statements and the like so make are punishable by
fine or imprisonment or both under section 1001 of Title 18 of
the United States Code and that such willful false statements

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may jeopardize the validity of the application or any patent issued thereon.

16th November 1999
DATE

HAROLD W. KROTO, PH.D.

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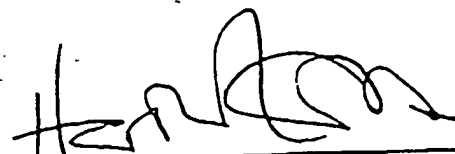
Exhibit 1

CURRICULUM VITAE I

Professor Sir Harold Kroto FRS,   Royal Society Research Professor

The School of Chemistry, Physics and Environmental Science,
The University of Sussex, Brighton, BN1 9QJ, UK

Tel   01 273 678329 desk
                 01 273 606755 Univ
Fax   01 273 677196 dept
email   kroto@sussex.ac.uk

Born 7th Oct 1939 Wisbech, Cambridgeshire, England.

Education
1947-58   Bolton School, Bolton, Lancashire.

1958-61   BSc, Sheffield, 1st class honours degree (Chemistry)

1961-64   PhD, Sheffield, *Electronic Spectroscopy of Unstable Molecules*; Supervisor: R N Dixon

1964-65   PDF, NRC (Ottawa) with D A Ramsay

1965-66   PDF, NRC (Ottawa) with C C Costain

1966-67   Memb. Tech. Staff, Bell Laboratories, Murray Hill, NJ (with Y H Pao, and D P Santry)

University Career (University of Sussex 1967-)
1967-68 (Tutorial Fellow); 1968-78   (Lecturer); 1978-85   (Reader)
1985-91 (Professor); 1991- (Royal Society Research Professor)

Awards
1981-82   Tilden Lecturer (Royal Society of Chemistry)
1990   Elected Fellow of the Royal Society
1991-   Royal Society Research Professorship
1992   International Prize for New Materials
                         (American Physical Society/IBM, with R F Curl and R E Smalley)
                 Italgas Prize for Innovation in Chemistry
                 Université Libre de Bruxelles (DHC)
                 University of Stockholm (PhDHC)
                 Longstaff Medal 1993 (Royal Society of Chemistry)
                 Academia Europaea (Member)
1993   University of Limburg(DHC)
1994   Hewlett Packard Europhysics Prize
                         (with D R Huffman, W Krätschmer and R E Smalley)
                 Moet Hennessy*Louis Vuitton *Science pour l'Art* Prize
1995   University of Sheffield (Hon Degree)
                 University of Kingston (Hon Degree)
1996   Knighthood, Nobel Prize for Chemistry (with R F Curl and R E Smalley)
1997   University of Sussex (Hon Degree)
                 University of Helsinki (DHC)

Extra-university administration
SRC   Millimetre Wave Telescope Sub-Committee 1977-81
SERC   Millimetre Wave Telescope Users'Committee 1981-85
SERC   Physical Chemistry Subcommittee 1987-90
SERC   Synchrotron Radiation Facility Committee 1987-90
SERC   Chemistry Committee 1988-91
IAU   Sub-group on Astrophysical Chemistry 1987-
MBI   Advisory Board of the Max Born Institute (Berlin) 1993-

RESEARCH

Main research areas:

I   Spectroscopy of Unstable Species and Reaction Intermediates
           (Infrared, Photoelectron, Microwave and Mass Spectrometry)

II.   Cluster Science
           (Carbon and Metal Clusters, Microparticles, Nanofibres)

III   Fullerenes
           (Chemistry, Physics and Materials Science)

IV   Astrophysics
           (Interstellar Molecules and Circumstellar Dust)

Research Highlights:

a)   Synthesis in 1976 of the first phoaphaalkenes (compounds containing the free carbon phosphorus double bond) in particular $CH_2 = PH$ (with N P C Simmons and J F Nixon, Sussex), Refs 1,7.

b)   Synthesis in 1976 of the first analogues of HCP, the phosphaalkynes which contain the carbon phoshorus triple bond - in particular CH_3CP (with N P C Simmons and J F Nixon, Sussex), Refs 2,7.

c)   The discovery (1976-8) of the cyanopolyynes, HC_nN (n = 5,7,9), in interstellar space (with D R M Walton A J Alexander and C Kirby (Sussex) and T Oka, L W Avery, N W Broten and J M MacLeod (NRC Ottawa)), Ref 4-6, based on microwave measurements made at Sussex, Refs 3,7.

d)   The discovery of C_{60}: Buckminsterfullerene in 1985 (with J R Heath, S C O'Brien, R F Curl and R E Smalley), Refs 8,13,15.

e)   The detection of endohedral metallofullerene complexes (with J R Heath, S C O'Brien, Q Zhang, Y Liu, R F Curl, F K Tittel and R E Smalley), Ref 9

f)   The prediction that C_{60} should be produced in combustion processes and might indicate how soot is formed (with Q L Zhang, S C O'Brien, J R Heath, Y Liu, R F Curl and R E Smalley) Ref 10

g)   The explanation of why C_{70} is the second stable fullerene (after C_{60}) and the discovery of the *Pentagon Isolation Rule* as a criterion for fullerene stability in general (Refs 11,13,15)

h)   The prediction of the tetrahedral structure of C_{28} and the possible stability of "tetravalent" derivatives such as $C_{28}H_4$ Refs 11,15.

i)   The prediction that giant fullerenes have quasi-icosahedral shapes and the detailed structure of concentric shell graphite microparticles (with K G McKay), Refs 12,13.

j)   The mass spectrometric identification and solvent extraction (with J P Hare and A Abdul-Sada) of C_{60} from arc processed carbon in 1990 - independently from and simultaneously with the Heidelberg/Tucson group; Refs 14,15.

k)   The chromatographic separation/purification of C_{60} and C_{70} and ^{13}C NMR measurements which provided unequivocal proof that these species had fullerene cage structures (with J P Hare and R Taylor, Sussex), Refs 14,15.

Meetings (director, organiser or co-orgnaisor)
- Brioni International Conferences 1988, 1990, 1993, ...
- Royal Society Discussion Meeting 1992
- Fullerene Symposium 1993 (Santa Barbara)
- Cursos de Verano (El Escorial) *Fullerenos* 1994

Editorial Boards
- *Chemical Society Reviews* 1986- (Chairman 1990-)
- *Zeitschrift fur Physik D* (Atoms Molecules and Clusters) 1992-
- *Carbon* (1992-)
- *J. Chem. Soc. Chem. Comm.* (1993-)

Research Details

University of Sheffield
1961-64   PhD in Free radical spectroscopy by flash photolysis

National Research Council
1964-65   Free radical spectroscopy by flash photolysis
1965-66   Microwave Spectroscopy

Bell Telephone Laboratories
1966-67   Raman Spectroscopy of Liquids, Quantum Chemistry

University of Sussex
1967-72   Free radical spectroscopy/flash photolysis
1967-73   Liquid phase interactions/Raman Spectroscopy
1970-   Unstable species/Microwave Spectroscopy
1972-90   Unstable species/Photoelectron Spectroscopy
1976-   Interstellar Molecules/Radioastronomy
1983-90   Unstable species/Fourier Transform IR Spectroscopy
1985-   Cluster Studies/Carbon, Metals
1990-   Fullerene Chemistry, Carbon nanostructures

Temporary Appointments (Visiting Professorships etc)

1974   Visiting Associate Professor, UBC Vancouver (3 months)
1976   Visiting Scientist, NRC Ottawa (3 wks)
1978   Visiting Scientist, NRC Ottawa (3 wks)
1981   Visiting Professor, USC (3 months).
1983   British Council Visitor, Inst Rudjer Boskovic (Zagreb)
1987   CNRS (1 month) Univ Paris Sud (Orsay)
1988-   Visiting Professor UCLA (Astronomy)
1996   Senior Visiting Research Fellow (UC Santa Barbara)

Extramural Activities
Sport
- Tennis and Squash for Sheffield University (1959-1964).
- University Athletics Union Finalists - Tennis (1962 and 1963)
- President of Athletics Council, Sheffield University (1963-64)

Television Film
- Chairman of Board of *VEGA SCIENCE TRUST*
- Executive producer of seven 1-hour Television Films of Royal Institution Discourses for Vega/BBCFocus

Graphic Art and Design
- Art Editor *Arrows* Sheffield University Arts Magazine 1962-64

PUBLICATIONS

240 research papers; book *Molecular Rotation Spectra* (Wiley 1975 - reprinted with a new preface Dover 1992)

Key Publications

1)   M J Hopkinson, H W Kroto, J F Nixon and N P C Simmons, 'The detection of unstable molecules by microwave spectroscopy: phospha-alkenes $CF_2=PH$, $CH_2=PCl$ and $CH_2=PH$', *J.C.S. Chem. Comm.*, 513-515 (1976).

2)   M J Hopkinson, H W Kroto, J F Nixon and N P C Simmons, 'The detection of the reactive molecule 1-phosphapropyne, CH_3CP, by microwave spectroscopy', *Chem. Phys. Letts.*, 42, 460-461 (1976).

3)   A J Alexander, H W Kroto and D R M Walton, 'The microwave spectrum, substitution structure and dipole moment of cyanobutadiyne, HC_5N', *J. Mol. Spectrosc.*, 62, 175-180 (1976).

4)   L W Avery, N W Broten, J M MacLeod, T Oka and H W Kroto, 'Detection of the heavy interstellar molecule cyanodiacetylene', *Astrophys. J.*, 205, L173-175 (1976).

5)   H W Kroto, C Kirby, D R M Walton, L W Avery, N W Broten, J M MacLeod and T Oka, 'The Detection of Cyanohexatriyne, HC_7CN, in Heiles' Cloud 2', *Astrophysics J.*, 219, L133-L137 (1978).

6)   N W Broten, T Oka, L W Avery, J M MacLeod and H W Kroto, 'The Detection of HC_9N in Interstellar Space', *Astrophys. J.*, 223, L105-107 (1978).

7)   H W Kroto, 'Semistable Molecules in the Laboratory and in Space', Royal Society of Chemistry Tilden Lecture; *Chem. Soc. Revs.*, 11, 435-491 (1982).

8)   H W Kroto, J R Heath, S C O'Brien, R F Curl and R E Smalley, 'C_{60}: Buckminsterfullerene', *Nature*, 318(No.6042), 162-163,(1985)

9)   J R Heath, S C O'Brien, Q Zhang, Y Liu, R F Curl, H W Kroto, F K Tittel and R E Smalley 'Lanthanum Complexes of Spheroidal Carbon Shells', *J. Am. Chem. Soc.*, 107, 7779-7780 (1985).

10)   Q L Zhang, S C O'Brien, J R Heath, Y Liu, R F Curl, H W Kroto and R E Smalley. 'Reactivity of large carbon clusters Spheroidal Carbon Shells and their possible relevance to the formation and morphology of soot', *J. Phys. Chem.*, 90, 525-528 (1986)

11)   H W Kroto, 'The Stability of the Fullerenes C_n (n = 24, 28, 32, 50, 60 and 70)', *Nature* 329, 529-531 (1987)

12)   H W Kroto and K McKay, 'The Formation of Quasi-icosahedral Spiral Shell Carbon Particles' *Nature*, 331, 328-331 (1988)

13)   H W Kroto   "Space, Stars, C_{60} and Soot", *Science*, 242, 1139-1145 (1988)

14)   R Taylor, J P Hare, A K Abdul-Sada, and H W Kroto, "Isolation, Separation and Characterisation of the Fullerenes C_{60} and C_{70}: The Third Form of Carbon." *J. Chem. Soc. Chem. Commun.*, 1423-1425 (1990)

15)   H W Kroto "C_{60}: Buckminsterfullerene, the Celestial Sphere that Fell to Earth", *Angewandte Chemie* 31, 111-129 (1992)

Winner of *Sunday Times* Book Jacket Design Competition 1963
Editor, design and layout of *Chemistry at Sussex*
          Cover design featured in *Modern Publicity 1979* (international annual of Graphic Design)
Publicity and logos for Chemical Society Meetings
Logo, letterheads for Science and Engineering at Sussex
Publicity, logo, letterheads, poster for BA Meeting 1983
New Scientist BA Advertisement
Logo and letterhead for Inorganic Biochemistry Discussion Group
Logo and letterhead 1990 for *Venture Research International*
          (Formerly *BP Venture Research*)
New Cover design and layout for *Chemical Society Reviews*

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Concise

Encyclopedia

of Science

&

Technology

Third Edition

Sybil P. Parker
Editor in Chief

McGraw-Hill, Inc.

Diagram of a typical aircraft fuel system.
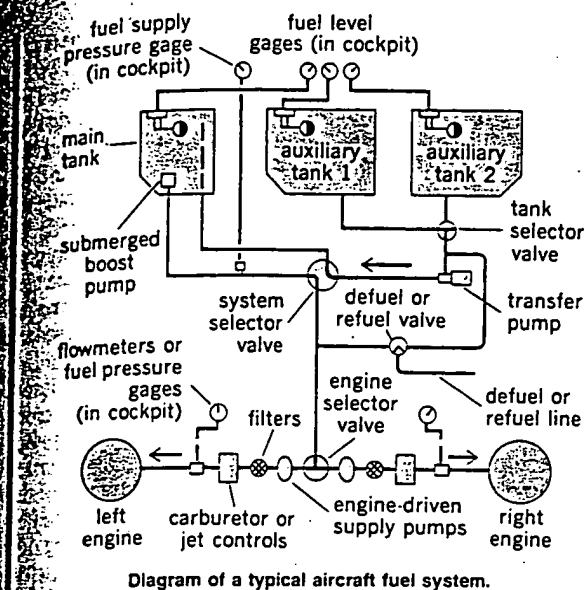
is usually such that all the fuel supply will pass to the engines by way of the main tank, which is refilled as necessary from the auxiliary tanks. In case of emergency, the system selector valve may connect the auxiliary tanks to the engines directly.   [F.C.M./J.A.B.]

Fugacity A function introduced by G. N. Lewis to facilitate the application of thermodynamics to real systems. Thus, when fugacities are substituted for partial pressures in the mass action equilibrium constant expression, which applies strictly only to the ideal case, a true equilibrium constant results for real systems as well.

The fugacity f_i of a constituent i of a thermodynamic system is defined by the following equation (where μ_i is the chemical

$$\mu_i = \mu_i^* + RT \ln f_i$$

potential and μ_i^* is a function of temperature only), in combination with the requirement that the fugacity approach the partial pressure as the total pressure of the gas phase approaches zero. At a given temperature, this is possible only for a particular value of μ_i^*, which may be shown to correspond to the chemical potential the constituent would have as the pure gas in the ideal gas state at 1 atm pressure. This definition makes the fugacity identical to the partial pressure in the ideal gas case. For real gases, the ratio of fugacity to partial pressure, called the fugacity coefficient, will be close to unity for moderate temperatures and pressures. At low temperatures and appropriate pressures, it may be as small as 0.2 or less, whereas at high pressures at any temperature it can become very large. See ACTIVITY (THERMODYNAMICS); CHEMICAL EQUILIBRIUM; CHEMICAL THERMODYNAMICS; GAS.   [P.J.B.]

Fullerene A molecule containing an even number of carbon atoms arranged in a closed hollow cage. The fullerenes were discovered as a consequence of astrophysically motivated chemical physics experiments that were interpreted by using geodesic architectural concepts. Fullerene chemistry, a new field that appears to hold much promise for materials development and other applied areas, was born from pure fundamental science. See CARBON.

In 1985, fifteen years after it was conceived theoretically, the molecule buckminsterfullerene (C_{60} or fullerene-60) was discovered serendipitously. Fullerene-60 (see illustration) is the archetypal member of the fullerenes, a set of hollow, closed-cage molecules consisting purely of carbon. The fullerenes can be considered, after graphite and diamond, to be the third well-defined allotrope of carbon.

In the fullerene molecule an even number of carbon atoms are arrayed over the surface of a closed hollow cage. Each atom is trigonally linked to its three near neighbors by bonds that delineate a polyhedral network, consisting of 12 pentagons and n hexagons. All 60 atoms in fullerene-60 are equivalent and lie on the surface of a sphere distributed with the symmetry of a truncated icosahedron. The 12 pentagons are isolated and interspersed symmetrically among 20 linked hexagons; that is, the symmetry is that of a modern soccerball. The molecule was named after R. Buckminster Fuller, the inventor of geodesic domes, which conform to the same underlying structural formula. Three of the four valence electrons of each carbon atom are involved in the sp^2 sigma-bonding skeleton, and the fourth p electron is one of 60 involved in a pi-delocalized molecular-orbital electron sea that covers the outside (exo) and inside (endo) surface of the molecule. The resulting cloud of pi electron density is similar to that which covers the surface of graphite; indeed, the molecule can be considered a round form of graphite. See ELECTRON CONFIGURATION; GRAPHITE.

Fullerene-60 behaves as a soft electrophile, a molecule that readily accepts electrons during a primary reaction step. It can accept three electrons readily and perhaps even more. The molecule can be multiply hydrogenated, methylated, ammonated, and fluorinated. It forms exohedral complexes in which an atom (or group) is attached to the outside of the cage, as well as endohedral complexes in which an atom [for example, lanthanum (La), potassium (K), or calcium (Ca)] is trapped inside the cage.
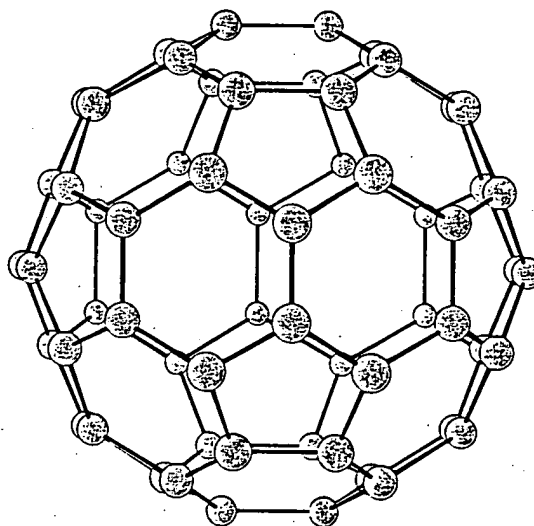
Structure of C_{60} (buckminsterfullerene).

Fullerene materials have been available for such a short time that applications are yet to be established. However, the properties already discovered suggest that there is likely to be a wide range of areas in which the fullerenes or their derivatives will have uses.

Fullerene-60 was discovered as a direct result of physicochemical investigations that simulated processes occurring in stars and in space. Consequently the likelihood that fullerenes, in particular fullerene-60, and analogs are present in space is a fascinating conjecture.   [H.W.K.]

Fuller's earth Any natural earthy material (such as clay materials) which decolorizes mineral or vegetable oils to a sufficient extent to be of economic importance. It has no mineralogic significance. The clay minerals present in fuller's earth may include montmorillonite, attapulgite, and kaolinite.
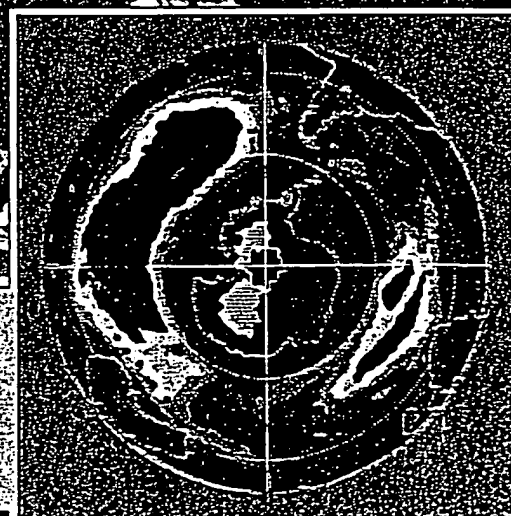
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nature

A NEW FORM OF CARBON

UNDERSTANDING ANTARCTIC OZONE DEPLETION

The cellular defect behind cystic fibrosis

Solid C₆₀: a new form of carbon

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A new form of pure, solid carbon has been syn-
thesized consisting of a somewhat disordered
hexagonal close packing of soccer-ball-shaped C_{60}
molecules. Infrared spectra and X-ray diffraction
studies of the molecular packing confirm that the
molecules have the anticipated 'fullerene' struc-
ture. Mass spectroscopy shows that the C_{70}
molecule is present at levels of a few per cent.
The solid-state and molecular properties of C_{60}
and its possible role in interstellar space can now
be studied in detail.

FOLLOWING the observation that even-numbered clusters of
carbon atoms in the range C_{30}–C_{100} are present in carbon
vapour[1], conditions were found[2-4] for which the C_{60} molecule
could be made dominant in the large-mass fraction of vapourized
graphite. To explain the stability of the molecule, a model was
proposed of an elegant structure in which the carbon atoms are
arranged at the 60 vertices of a truncated icosahedron, typified
by a soccer ball. The structure, dubbed buckminsterfullerene[2]
because of its geodesic nature, has been the subject of several
theoretical stability tests[5,6] and has been discussed widely in the
literature. Calculations of many physical properties have been
made, including electron energies[7-9], the optical spectrum[9],
vibrational modes[10-15], and the electric and magnetic
properties[16,17]. There has been speculation on the possible
chemical and industrial uses of C_{60} (ref. 2), and on its importance
in astrophysical environments[18-20]. Until now, it has not been
possible to produce sufficient quantities of the material to permit
measurement of the physical properties, to test the theoretical
calculations, or to evaluate the possible applications.

Some of us have recently reported evidence[21,22] for the pres-
ence of the C_{60} molecule in soot condensed from evaporated
graphite. The identification was based primarily on the observed
isotope shifts of the infrared absorptions when ^{12}C was replaced
by ^{13}C, and on comparison of the observed features with theoreti-
cal predictions. The measured infrared and ultraviolet absorp-
tion bands were superimposed on a rather large continuum
background absorption from the graphitic carbon which com-
prised ≥95% of the sample. Here we report how to extract the
carrier of the features from the soot, how to purify it, and
evidence that the material obtained is in fact primarily C_{60}.

Method of production

The starting material for our process is pure graphitic carbon
soot (referred to below as simply soot) with a few per cent by
weight of C_{60} molecules, as described in refs 21, 22. It is produced
by evaporating graphite electrodes in an atmosphere of
~100 torr of helium. The resulting black soot is gently scraped
from the collecting surfaces inside the evaporation chamber and
dispersed in benzene. The material giving rise to the spectral
features attributed to C_{60} dissolves to produce a wine-red to
brown liquid, depending on the concentration. The liquid is
then separated from the soot and dried using gentle heat, leaving
a residue of dark brown to black crystalline material. Other
non-polar solvents, such as carbon disulphide and carbon tetra-
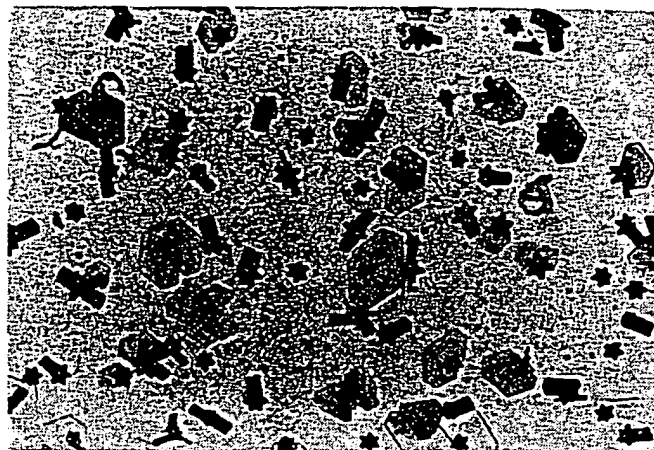chloride, can also dissolve the material. An alternative con-

FIG. 1 Transmission micrograph of typical crystals of the C_{60} showing thin
platelets, rods and stars of hexagonal symmetry.

centration procedure is to heat the soot to 400 °C in a vacuum
or in an inert atmosphere, thus subliming the C_{60} out of the
soot (W. Schmidt, personal communication). The sublimed coat-
ings are brown to grey, depending on the thickness. The refrac-
tive index in the near-infrared and visible is about two. To purify
the material, we recommend removing the ubiquitous hydrocar-
bons before the concentration procedure is applied (for example,
by washing the initial soot with ether). Thin films and powder
samples of the new material can be handled without special
precautions and seem to be stable in air for at least several
weeks, although there does seem to be some deterioration with
time for reasons that are as yet unclear. The material can be
sublimed repeatedly without decomposition. Using the
apparatus described, one person can produce of the order of
100 mg of the purified material in a day.

Studies by optical microscopy of the material left after
evaporating the benzene show a variety of what appear to be
crystals—mainly rods, platelets and star-like flakes. Figure 1
shows a micrograph of such an assemblage. All crystals tend to
exhibit six-fold symmetry. In transmitted light they appear red
to brown in colour; in reflected light the larger crystals have a
metallic appearance whereas the platelets show interference
colours. The platelets can be rather thin and are thus ideally
suited for electron-diffraction studies in an electron microscope
(see the inset in Fig. 3).

Mass spectroscopy

The material has been analysed by mass spectrometry at several
facilities. All mass spectra have a strong peak at mass 720 a.m.u.,
the mass of C_{60}. Significant differences in the spectra occur only
at masses lower than 300 a.m.u. Most of these differences seem
to originate from the different ionization techniques and in the
different methods of desorbing molecules from the sample. Mass
spectra recorded at low and high resolution are shown in Fig.
2. The spectra were obtained using a time-of-flight secondary-ion
mass spectrometer[23] and a C_{60}-coated stainless-steel plate. In
the mass range above 300 a.m.u., the spectrum is dominated by
C_{60} ions and its fragments (even-numbered clusters of atomic
carbon), and C_{70} ions. In this sample, the ratio of C_{70} to C_{60} is
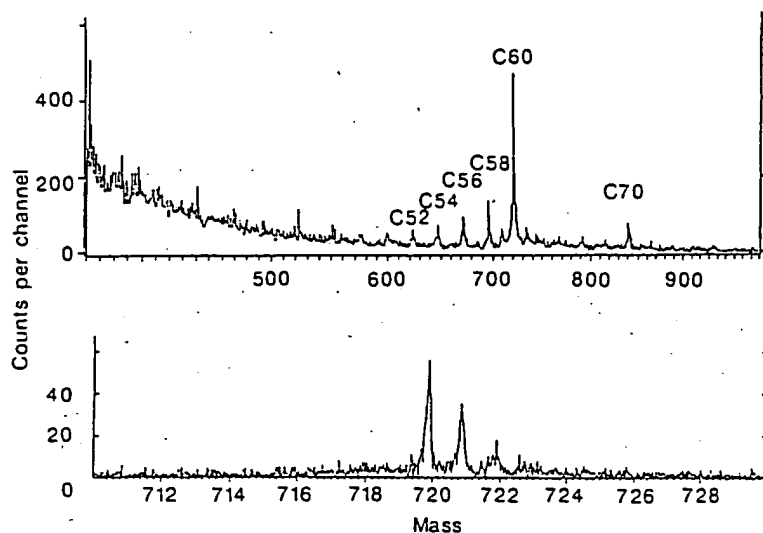
FIG. 2 Low-resolution (top) and high-resolution time-of-flight mass spectra of positive ions obtained from coatings of solid C_{60}. A 5-keV Ar^+ ion beam was used to sputter and ionize the sample. The isotope pattern (bottom) is approximately that expected for C_{60} molecules composed of ^{12}C and ^{13}C isotopes of natural abundance.

~0.1. The high-resolution mass spectrum shows approximately the expected isotope pattern for C_{60}. The increasing background in the low-resolution mass spectrum is not produced by the sample—such backgrounds also occur in blank measurements on uncoated stainless-steel substrates.

So far, the cleanest mass spectra have been obtained when the material was evaporated and ionized in the vapour phase by electrons. In such spectra the low-mass background is substantially reduced and the entire mass spectrum is dominated by C_{60} ions and its fragments. The ratio of C_{70} to C_{60} in these mass spectra is ~0.02 and seems to be smaller than that shown in Fig. 2. Both ratios are of the order of those reported from laser-evaporation experiments[2,3]. We assume, as previously suggested[24], that the C_{70} molecule also has a closed-cage structure, either elongated[24] or nearly spherical[25]. Further details of the mass spectroscopy of the new material will be published elsewhere.

Structure

To determine if the C_{60} molecules form a regular lattice, we performed electron and X-ray diffraction studies on the individual crystals and on the powder. A typical X-ray diffraction pattern of the C_{60} powder is shown in Fig. 3. To aid in comparing the electron diffraction results with the X-ray results we have inset the electron diffraction pattern in Fig. 3. From the hexagonal array of diffraction spots indexed as shown in the figure, a d spacing of 8.7 Å was deduced corresponding to the (100) reciprocal lattice vector of a hexagonal lattice. The

most obvious correspondence between the two types of diffraction is between the peak at 5.01 Å of the X-ray pattern and the (110) spot of the electron diffraction pattern, which gives a spacing of ~5.0 Å. Assuming that the C_{60} molecules are behaving approximately as spheres stacked in a hexagonal close-packed lattice with a c/a ratio of 1.633, d spacings can be calculated. The results are shown in Table 1. The values derived from this interpretation are $a = 10.02$ Å and $c = 16.36$ Å. The nearest-neighbour distance is thus 10.02 Å. For such a crystal structure the density is calculated to be 1.678 g cm^{-3}, which is consistent with the value of 1.65 ± 0.05 g cm^{-3} determined by suspending crystal samples in aqueous $GaCl_3$ solutions of known densities. Although the agreement shown in Table 1 is good, the absence of the characteristically strong (101) diffraction of the hexagonal close-packed structure, and the broad continuum in certain regions suggest that the order is less than perfect. Further, X-ray diffraction patterns from carefully grown crystals up to 500 μm in size with well developed faces yielded no clear spot pattern (in contrast to the electron diffraction pattern on micrometre-sized crystals). It therefore appears that these larger crystals do not exhibit long-range periodicity in all directions.

A likely explanation for these facts lies in the disordered stacking of the molecules in planes normal to the c axis. It is well known that the positions taken by spheres in the third layer of stacking determines which of the close-packed structures occurs, the stacking arrangement in a face-centred cubic structure being ABCABC... whereas that in a hexagonal close-
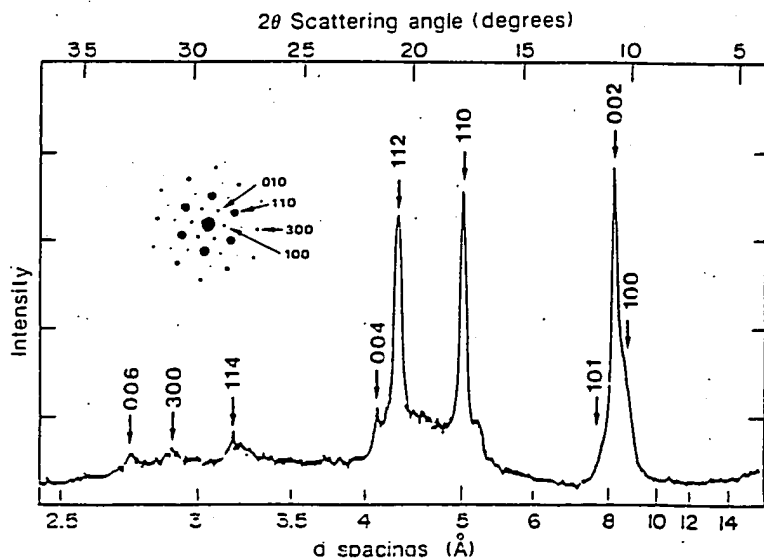

FIG. 3 X-ray diffraction pattern of a microcrystalline powder of C_{60}. Inset (upper left) is a single-crystal electron diffraction pattern indexed with Miller indices compatible with the X-ray pattern. The pattern is from a thin platelet such as those in Fig. 1 with the electron beam perpendicular to the flat face.

TABLE 1   X-ray diffraction results

Measured 2θ (deg)	Measured d spacing (Å)	Calculated d spacing (Å)	Assignment (hkl)
10.2 shoulder	8.7	8.68	(100)
10.81	8.18	8.18	(002)
		7.68	(101)
17.69	5.01	5.01	(110)
20.73	4.28	4.28	(112)
21.63	4.11	4.09	(004)
28.1	3.18	3.17	(114)
30.8	2.90	2.90	(300)
32.7	2.74	2.73	(006)

Assignments for a hexagonal lattice using $a = 10.02$ Å, $c = 16.36$ Å. $(1/d^2) = \frac{4}{3}[(h^2 + hk + k^2)/a^2] + l^2/c^2$.

packed structure is ABABAB ... If the stacking sequence varies, the X-ray lines owing to certain planes will be broadened by the disorder whereas other lines will remain sharp. Such disordered crystalline behaviour was observed long ago in the hexagonal close-packed structure of cobalt[26-28] where X-ray diffraction lines such as (101), (102) and (202) were found to be substantially broadened by the stacking disorder. Reflections from planes such as (002) remain sharp because these planes have identical spacings in the face-centred cubic and hexagonal close-packed structures. For the planes producing broadened diffraction peaks because of this kind of disorder, the following condition for the Miller indices (hkl) has been shown to apply[27,29]: $h - k = 3t \pm 1$ (where t is an integer) and $l \neq 0$. None of these broadened reflections are apparent in the X-ray pattern of Fig. 3. This may explain the weakness of the characteristically strong (101) peak. Whether or not this stacking disorder is related to the presence of the possibly elongated C_{70} molecule has yet to be determined.

In small crystals at least, the C_{60} molecules seem to assemble themselves into a somewhat ordered array as if they are effectively spherical, which is entirely consistent with the hypothesis that they are shaped like soccer balls. The excess between the nearest-neighbour distance (10.02 Å) and the diameter calculated for the carbon cage itself (7.1 Å) must represent the effective van der Waals diameter set by the repulsion of the π electron clouds extending outward from each carbon atom. Because the van der Waals diameter of carbon is usually considered to be 3.3–3.4 Å the packing seems a little tighter than one might expect for soccer-ball-shaped C_{60} molecules. The reason for this has not yet been determined.

In summary, our diffraction data imply that the substance isolated is at least partially crystalline. The inferred lattice constants, when interpreted in terms of close-packed icosahedral C_{60}, yield a density consistent with the measured value. Further evidence that the molecules are indeed buckminsterfullerene and that the solid primarily consists of these molecules comes from the spectroscopic results.

Spectroscopy

The absorption spectra of the graphitic soot[21,22] showed evidence for the presence of C_{60} in macroscopic quantities. Following the purification steps described above the material can be studied spectroscopically with the assurance that the spectra are dominated by C_{60}, with some possible effects from C_{70}. Samples were prepared for spectroscopy by subliming pure material onto transparent substrates for transmission measurements. Depending on the pressure of helium in the sublimation chamber, the nature of the coatings can range from uniform films (at high vacuum) to coatings of C_{60} smoke (sub-micrometre microcrystalline particles of solid C_{60}) with the particle size depending to some extent on the pressure.

Figure 4 shows the transmission spectrum of an ~2-μm-thick C_{60} coating on a silicon substrate. The infrared bands are at the same positions as previously reported[21,22], with the four most
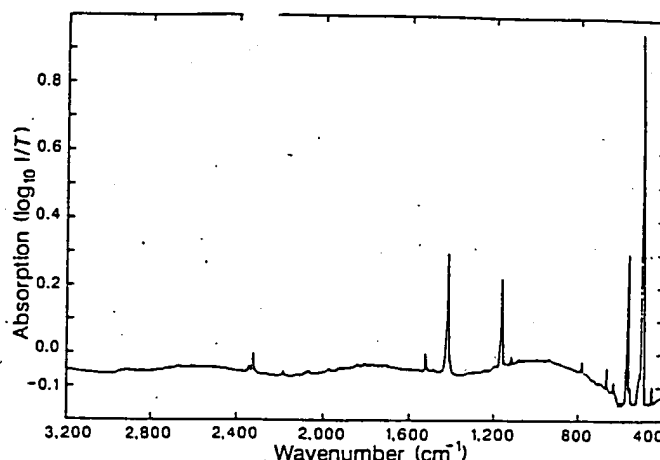

FIG. 4 Infrared absorption spectrum of a coating ~2 μm thick, of solid C_{60} on a silicon substrate, referenced to a clean silicon substrate. Apparent negative absorptions are due to the coating acting in part as a non-reflecting layer.

intense lines at 1,429, 1,183, 577 and 528 cm^{-1}; here, however, there is no underlying continuum remaining from the soot. In many of our early attempts to obtain pure C_{60}, there was a strong band in the vicinity of 3.0 μm, which is characteristic of a CH-stretching mode. After much effort this contaminant was successfully removed by washing the soot with ether and using distilled benzene in the extraction. The spectrum in Fig. 4 was obtained when the material cleaned in such a manner was sublimed under vacuum onto the substrate. The spectrum shows very little indication of CH impurities. Vibrational modes to compare with the measured positions of the four strong bands have been calculated by several workers[10-15]. As noted previously, the presence of only four strong bands is expected for the free, truncated icosahedral molecule with its unusually high symmetry. Also present are a number of other weak infrared lines which may be due to other causes, among which may be absorption by the C_{70} molecule or symmetry-breaking produced (for example) by isotopes other than ^{12}C in the C_{60} molecule or by mutual interaction of the C_{60} molecules in the solid. Weaker features at ~2,330 and 2,190 cm^{-1}, located in the vicinity of the free CO_2 and CO stretching modes, may imply some attachment of the CO_2 or CO to a small fraction of the total number of C_{60} molecules. Another notable feature is the peak at 675 cm^{-1}, which is weak in the thin-film substrates but almost as strong as the four main features in the crystals. We suspect that this vibrational mode may be of solid state rather than molecular origin.
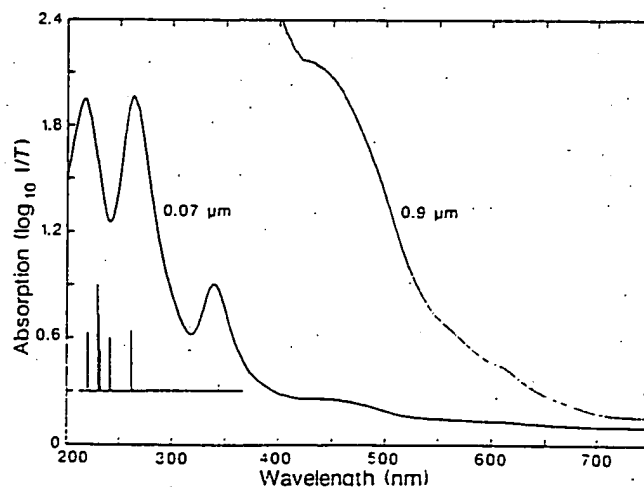

FIG. 5 Visible–ultraviolet absorption spectra of two thicknesses of solid C_{60} on quartz. The calculated[3] positions and relative oscillator strengths for allowed transitions of C_{60} are shown on the bottom.

Figure 5 shows an absorption spectrum taken on a uniform film coated on a quartz glass substrate. The ultraviolet features are no longer obscured by the graphitic carbon background as in our previous spectra[22]. Broad peaks at 216, 264 and 339 nm dominate the spectra. Weaker structures show up in the visible, including a plateau between ~460 and 500 nm and a small peak near 625 nm. At the bottom of Fig. 5 we have shown positions and relative oscillator strengths taken from Larsson, Volosov and Rosén[9] calculated for the C_{60} molecule. They also reported a variety of forbidden bands with the lowest energy ones in the vicinity of 500 nm. There seems to be a rough correspondence between our measurements on solid films and the allowed transitions predicted for the molecule. The possibility exists, however, that one or more of the absorption features shown in Fig. 5 are due to C_{70}. We still do not observe a band at 386 nm in our films, as observed[30] using a laser depletion spectroscopy method and attributed to the C_{60} molecule. Quite similar spectra to that in Fig. 5 have been recorded for microcrystalline coatings deposited at helium pressures of 100 torr, for example. The peaks occur at the slightly shifted positions of 219, 268 and 345 nm.

Possible interstellar dust

The original stimulus for the work[2] that led to the hypothesis of the soccer-ball-shaped C_{60} molecule, buckminsterfullerene, was an interest in certain unexplained features in the absorption and emission spectra of interstellar matter. These include an intense absorption band at 217 nm which has long been attributed to small particles of graphite[31], a group of unidentified interstellar absorption bands in the visible that have defied

explanation for more than 70 years[31,32], and several strong emission bands attributed to polycyclic aromatic hydrocarbons[33,34]. Based on the visible and infrared absorption spectra of Figs 4 and 5, we do not see any obvious matches with the interstellar features. The ultraviolet band at 216–219 nm has a similar peak wavelength to an interstellar feature, although the other strong bands of the spectrum have no interstellar counterparts. As the influence of C_{70} absorptions on the spectrum is not yet known, a conclusive comparison with the 217-nm interstellar band is difficult. We note that the visible–ultraviolet spectrum presented here is characteristic of a solid, rather than of free molecules. In addition, these new results do not relate directly to absorption in the free C_{60}^+ molecular ion, which has been envisaged[19] to explain the diffuse interstellar bands. Nevertheless, these data should now provide guidance for possible infrared detection of the C_{60} molecule, if it is indeed as ubiquitous in the cosmos as some have supposed.

Summary

To our method for producing macroscopic quantities of C_{60}, we have added a method for concentrating it in pure solid form. Analyses including mass spectroscopy, infrared spectroscopy, electron diffraction and X-ray diffraction leave little doubt that we have produced a solid material that apparently has not been reported previously. We call the solid fullerite as a simple extension of the shortened term fullerene, which has been applied to the large cage-shaped molecules typified by buckminsterfullerene (C_{60}). The various physical and chemical properties of C_{60} can now be measured and speculations concerning its potential uses can be tested. □

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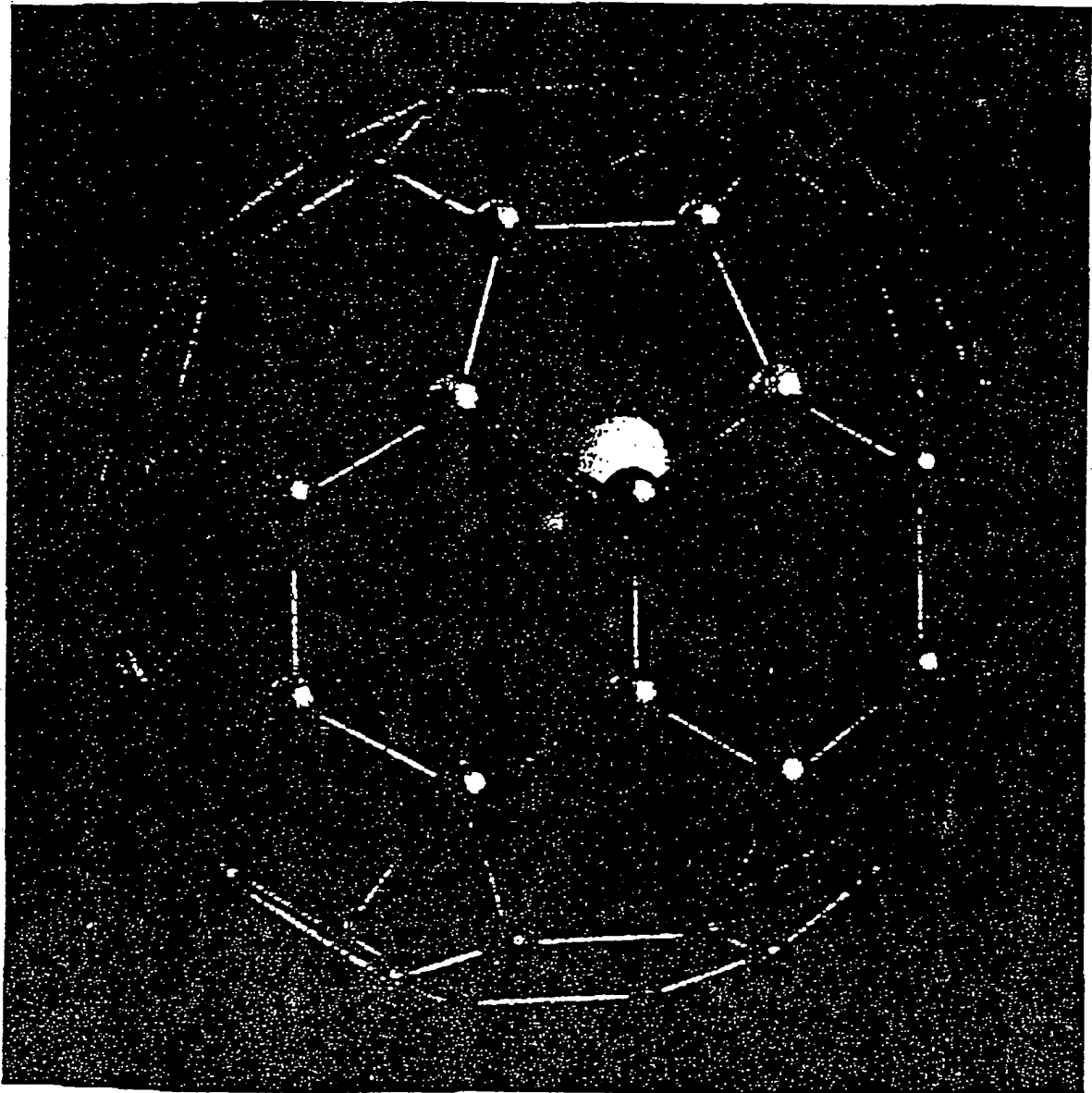
SCIENTIFIC AMERICAN

4

Remnants of a planet that failed to form.

Still no technological fix for oil spills.

What made higher life-forms possible?

Buckyball, the third form of pure carbon, cages an atom in its lattice.

Fullerenes

These cagelike molecules constitute the third form of pure carbon (the other two are diamond and graphite). C₆₀, the archetype, is the roundest molecule that can possibly exist

by Robert F. Curl and Richard E. Smalley

In May of 1990 Wolfgang Krätschmer and his student Konstantinos Fostiropoulos carefully mixed a few drops of benzene with a specially prepared carbon soot. The clear solvent turned red.

Excitedly, the two workers for the Max Planck Institute for Nuclear Physics in Heidelberg telephoned their collaborators, Donald Huffman and Lowell Lamb of the University of Arizona in Tucson, who quickly repeated the experiment. The excitement continued as the two groups communicated daily by telephone and fax, exchanging measurements of the material—its infrared and ultraviolet spectra, its X-ray diffraction pattern and its mass spectrograph. Yes, the values all matched those predicted for the 60-atom carbon cluster buckminsterfullerene.

Even though some theorists had argued that this hollow, soccerball-shaped molecule should be detectable in abundance in such everyday circumstances as a candle flame, the German-American team had actually found it, succeeding where all others had failed. They were the first to observe this roundest of all round molecules, and they knew that chemistry books and encyclopedias would never be quite the same. Now there were three known forms of pure carbon: the network solids, diamond and graphite, and a new class of discrete molecules—the fullerenes.

When we heard of this breakthrough a few months later in Texas, we celebrated with champagne all around. For although we had to some extent been scooped, we had been vindicated as well. Five years earlier we had had our own Eureka! experience. Together with our colleague Harold W. Kroto of the University of Sussex and our students James R. Heath and Sean C. O'Brien, we had found that C₆₀ could be made in a uniquely stable form simply by laservaporizing graphite in a pulsed jet of helium. We had gone on to propose that this extraordinary stability could be explained by a molecular structure having the perfect symmetry of a soccerball. Because the architectural principle also underlies the geodesic dome invented by the American engineer and philosopher R. Buckminster Fuller, we named it buckminsterfullerene, or buckyball for short.

In addition to C₆₀, another molecule, C₇₀, appeared to be quite special in these early experiments. We soon found that the stability of C₇₀ could be understood if the molecule had also taken the form of a geodesic dome. As Fuller had pointed out, all such domes can be considered networks of pentagons and hexagons. The 18th-century Swiss mathematician Leonhard Euler calculated that any such object must have precisely 12 pentagons in order to close into a spheroid, although the number of hexagons can vary widely. The soccerball structure of C₆₀ has 20 hexagons, whereas the structure we proposed for C₇₀ has 25, producing a shape reminiscent of a rugby ball.

In fact, we had found that all the even-numbered carbon clusters greater than about 32 atoms in size were remarkably stable (although less so than 60 or 70), and the evidence soon led us to postulate that all these molecules had taken the structure of geodesic domes. Again, in honor of Fuller, it seemed fitting to term this entirely new class of molecules the "fullerenes."

We later learned that such molecules had already been imagined. David E. H. Jones, writing under the pseudonym "Daedalus" in the *New Scientist* in 1966, had conceived of a "hollow molecule" made of curled-up graphitic sheets. Others had predicted the stability of C₆₀ from calculations and tried—unsuccessfully—to synthesize it. We, however, were apparently the first to discover that the material could form spontaneously in a condensing carbon vapor.

Although our evidence was sound and our conclusions were supported by extensive further experiments and theoretical calculations, we could not collect more than a few tens of thousands of these special new molecules. This amount was plenty to detect and probe with the sophisticated techniques available in our laboratory, but there was not enough to see, touch or smell. Our evidence was indirect, much as it is for physicists who study antimatter. For now, the fullerenes existed only as fleeting signals detected in our exotic machines. But as chemists, we knew that the new material ought to be perfectly stable. Unlike antimatter, the geodesic forms of carbon should be quite safe to hold in one's bare hand. All we had to do was make more of them—billions and billions more.

Thus, for five years, we had been searching for a method of producing viable amounts of the stuff. We called our efforts "the search for the yellow vial" because quantum calculations for such a soccerball-shaped carbon molecule suggested it would absorb light strongly only in the far violet part of the spectrum. We were not alone. Our initial "soccerball"

ROBERT F. CURL and RICHARD E. SMALLEY of Rice University have collaborated for the past seven years in research on carbon and semiconductor clusters in supersonic beams. Curl is a professor in, and chairman of, the department of chemistry. Smalley is the Gene and Norman Hackerman Professor of Chemistry and a professor of physics. For the past five years, he has also served as the chairman of the Rice Quantum Institute.

HYPERFULLERENE STRUCTURE called a Russian egg is expected to form along with ordinary fullerenes in a laser-vaporized carbon plume. Shown here is the most symmetric form: a C₆₀ at the core is encapsulated by fullerenes having 240, 540 and 960 atoms. This process could continue indefinitely to produce a macroscopic particle whose pentagons are in icosahedral alignment.

proposal, published in *Nature* in 1985, had made the quest one of the hottest in chemistry.

In our laboratory we collected the sooty carbon produced by the vaporization laser while using various chemical techniques to detect the presence of C_{60}. We slurried the soot in benzene, for example, and looked for a yellow color. But the solution in our test tubes stayed clear, with boring black soot sitting on the bottom. The community of cluster chemists ran many more sophisticated experiments but achieved no better result.

Many gave up hope of ever seeing the yellow vial. They reasoned that although the fullerenes may be stable, it was too hard to separate them from the other sooty material being produced in the vaporization experiments. Per-

haps, the workers said, some dedicated chemist might one day extract a few micrograms with some special solvent, but no one seriously expected C_{60} to be available in bulk anytime soon.

In the end, the breakthrough was made not by chemists but by physicists working in a totally different area. Huffman, Krätschmer and their students had been engaged for decades in a study of interstellar dust, which they assumed to consist mainly of particles of carbon (the most common particle-forming element). They therefore modeled the phenomenon in the laboratory by vaporizing carbon and condensing it in as many ways as possible. Optical tests figured in most of the studies. (Virtually all that is known of the interstellar dust stems from obser-

vations of how it absorbs and scatters starlight.)

In 1983 the physicists tried evaporating a graphite rod by resistive heating in an atmosphere of helium. They noticed that when the helium pressure was just right (about a seventh of an atmosphere), the dust strongly absorbed wavelengths in the far ultraviolet region, creating a peculiar, double-humped spectrum [see bottom illustration on page 58]. Most observers would have missed the two blips on the screen, but not Huffman and Krätschmer: they had studied spectra of carbon dust for years without encountering such an effect. They dubbed it their "camel" sample and wondered what it meant.

Nearly three years later, in the late fall of 1985, Huffman read in *Nature* of

C_{60}
(BUCKMINSTERFULLERENE)

C_{70}

"BUCKYBABIES"

C_{50}

C_{44}

C_{32}

"FUZZYBALL," or $C_{60}H_{60}$, is a predicted form of fully hydrogenated C_{60}: buckminsterfullerane.

"BUNNYBALL," or $C_{60}(OsO_4)$ (4-TERT-BUTYLPYRIDINE)$_2$, was synthesized by a team led by Joel M. Hawkins of the University of California at Berkeley.
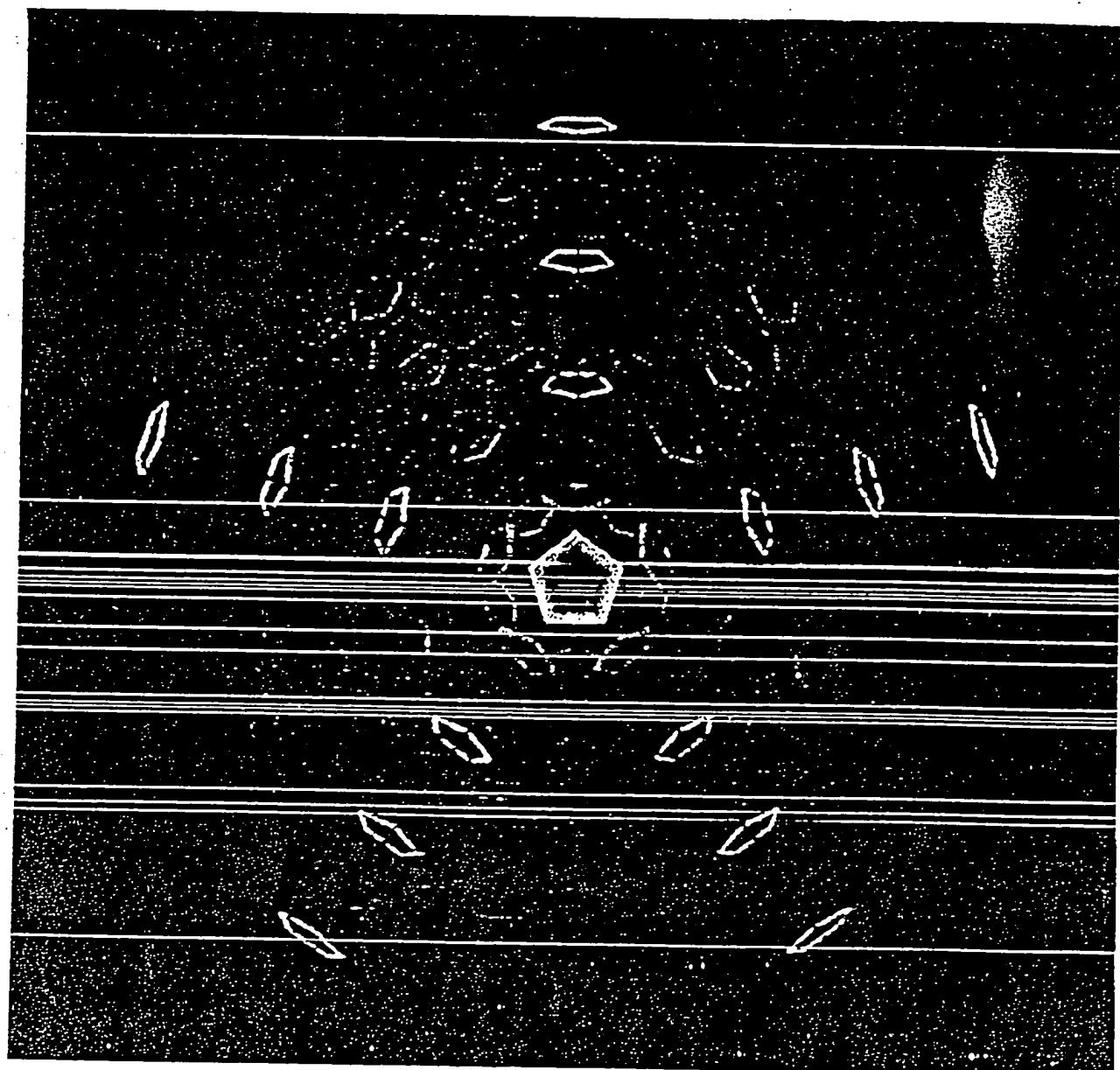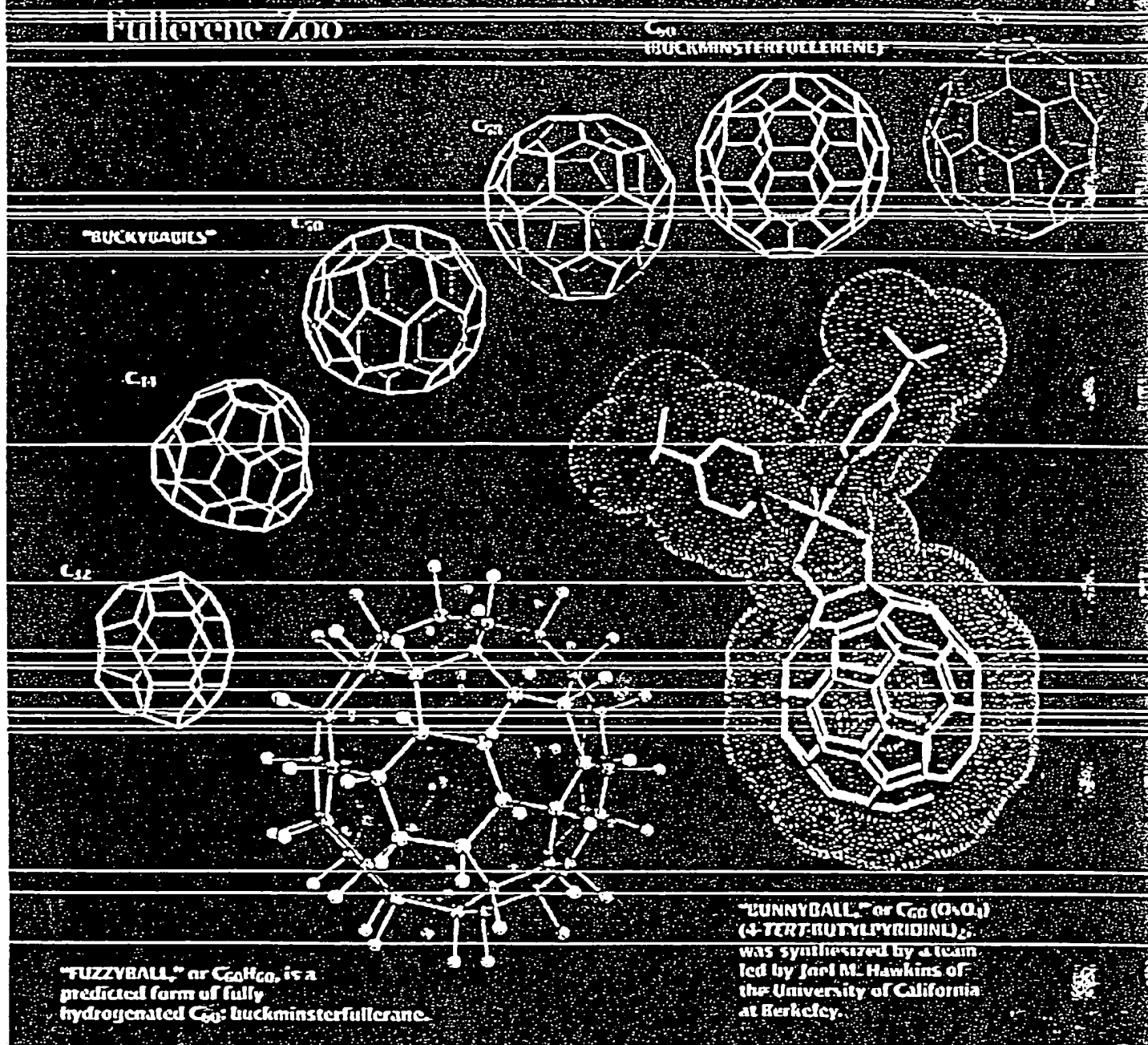
our discovery of C_{60} and began to wonder if a hollow soccerball molecule might be the cause of the double hump. Yet this explanation seemed too good to be true, for it required that C_{60} account for a significant portion of the sample. Why would so much of the carbon end up in such perfectly symmetric cages? What did the helium do to make it possible? The seeming unlikeliness of this hypothesis, together with some difficulty in reproducing the experiment, led the researchers to put the project on the back burner.

By 1989, however, Huffman and Krätschmer had become convinced that the C_{60} hypothesis ought to be reexamined. They renewed their interest in the camel sample, readily reproducing the results of the 1983 experiments. This time their attention turned to measuring the sample's absorption of infrared light—the wavelengths that interact with the vibrational motion of molecules—in order to test the results against theoretical predictions that had by now been made for soccerball C_{60}. These predictions held that of the 174

vibrational modes of this putative molecule, only 46 would be distinct, and only four would appear in the infrared range. To their surprise, they found the camel sample did display four sharp infrared absorption lines, and they verified that the lines were present only in carbon dust produced in the special camel way. This finding provided striking evidence that C_{60} might be present in abundance.

Influenced by their background in physics, the workers initially chose to test their hypothesis by a rather in-

GIANT FULLERENES

C_{240}

C_{540}

C_{960}
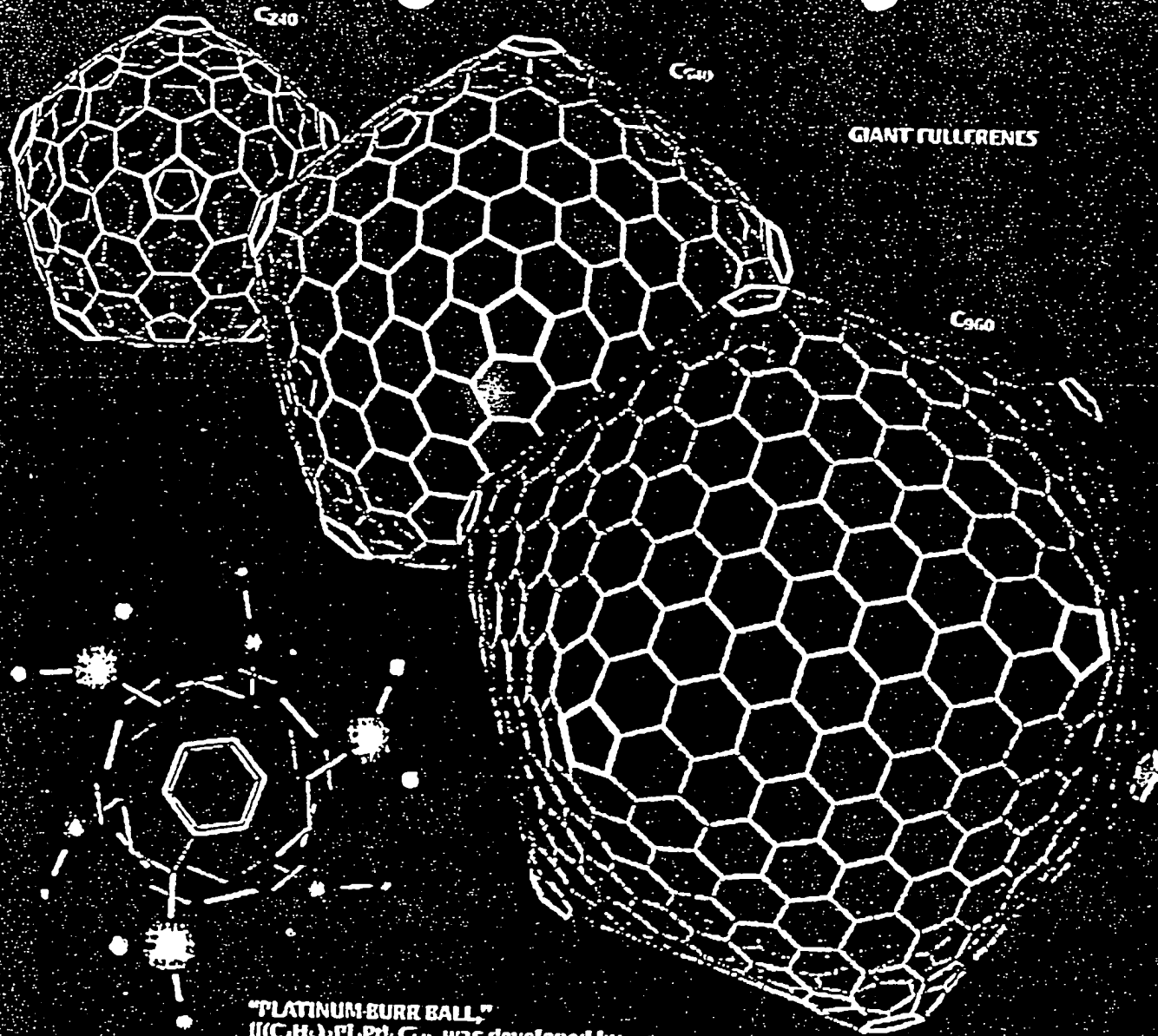
"PLATINUM-BURR BALL,"
$[[(C_2H_5)_3P]_2Pt]_6C_{60}$, was developed by
Paul J. Fagan and Joseph C. Calabrese
of the Central Research and
Development Department of Du Pont
Company. The C_2H_5 complexes are left
out for simplicity's sake.

volved route. They prepared a sample from pure ^{13}C, a heavy isotope of carbon, and verified that the extra mass shifted the four infrared bands in the way expected for so large a molecule composed exclusively of carbon. Ultimately, however, they realized that the simplest assay followed a basic dictum of organic chemistry: like dissolves like. Should their sample dissolve in an aromatic solvent, such as benzene, this would support the predicted aromaticity of C_{60}. Because benzene molecules take the shape of a ring of carbon at-

oms. C_{60} would thus be seen as a kind of spherical benzene.

When the Kratschmer-Huffman group finally added benzene to their camel sample and saw the color red develop, they realized they were looking at the first concentrated solution of fullerenes ever seen. They evaporated the solvent and found that tiny crystals remained, which readily redissolved. These crystals could be sublimed under a vacuum near 400 degrees Celsius and condensed on a cold microscope slide to form smooth films of solid materials,

which Kratschmer and Huffman christened "fullerite."

In thin layers these films were yellow (a fact that those of us at Rice University who searched for a "yellow vial" find highly gratifying). Although it took a while to obtain precise numbers, it is now known that carbon dust prepared in the camel way produces an extractable fullerene mixture made up of roughly 75 percent C_{60} (the soccerball), 23 percent C_{70} (the rugby ball) and a grab bag of larger fullerenes.

Here was a new form of pure, solid
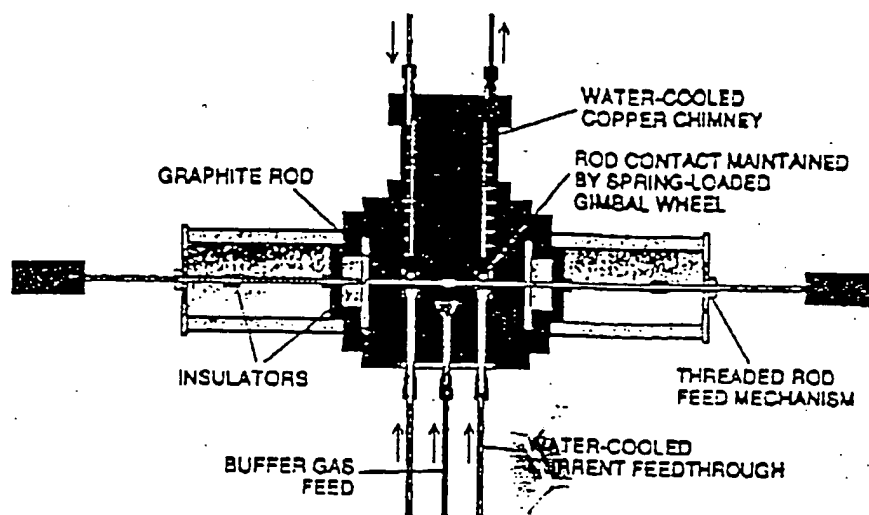
FULLERENE FACTORY makes macroscopic samples in a carbon arc. The arc—a refinement of an apparatus developed by Wolfgang Krätschmer and Donald Huffman—frees carbon atoms that coalesce into sheets. Inert helium holds the sheets near the arc long enough for them to close in on themselves, forming fullerenes.
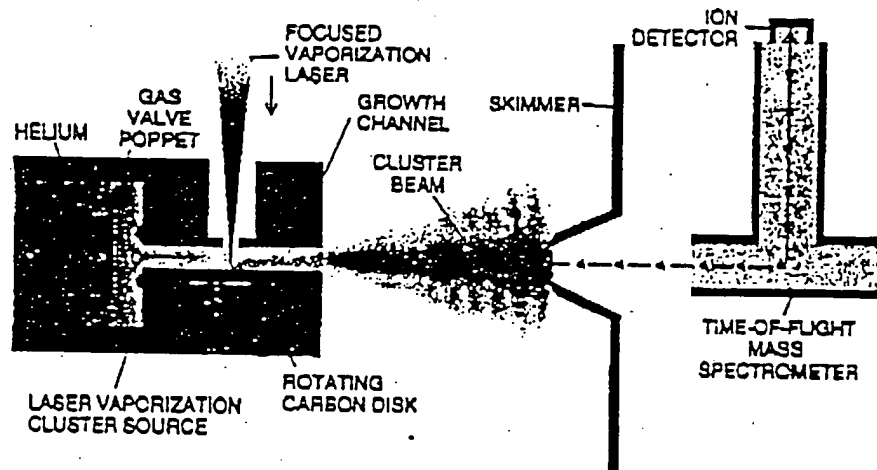
CLUSTER GENERATOR designed by one of the authors (Smalley) produced the first evidence that fullerenes can form from carbon vapor. A pulsed laser vaporizes carbon: a gust of helium then sweeps the vapor into a supersonic beam whose expansion cools the atoms, condensing them.
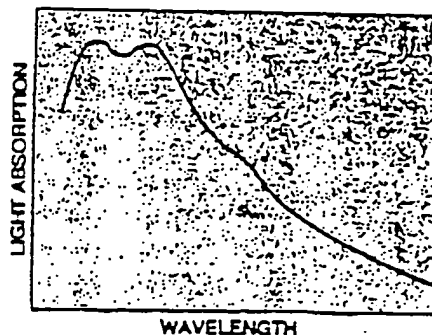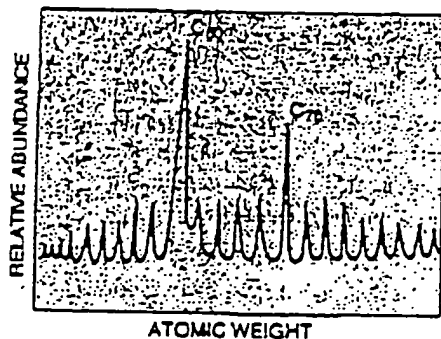
CRUCIAL GRAPHS: In 1985 the cluster-beam generator showed many even-numbered carbon clusters, especially C_{60}, suggesting that these species are particularly stable. The humped ultraviolet absorption spectrum led Krätschmer and Huffman to dub it the "camel" sample: in 1990 it was shown to contain C_{60}.

carbon. It is the only pure, finite form. The other two, diamond and graphite, are actually infinite network solids. In the real world, one usually deals with hunks of diamond cut out of larger bulk crystals. Under normal conditions, the surfaces of such a piece are instantly covered with hydrogen, which ties up the dangling surface bonds. Graphite is much the same. No piece of diamond, therefore, can ever be truly pure under normal conditions. The fullerenes, on the other hand, need no other atoms to satisfy their chemical bonding requirements on the surface. In this sense, the fullerenes are the first and only stable forms of pure, finite carbon.

Once the Krätschmer-Huffman results were announced at a conference in Konstanz, Germany, in early September 1990, the race was on. The study of C_{60} and the fullerenes had been the province of the few select groups that had something like our elaborate and expensive laser-vaporization cluster-beam apparatus. Now Krätschmer and Huffman had opened the field to anyone who could procure a thin rod of carbon, a cheap power supply, a bell-jar vacuum chamber and a few valves and gauges. Everybody could play.

Within a few months, many groups were making their own fullerenes. Physicists, chemists and materials scientists thus began an interdisciplinary feeding frenzy that continues to intensify as this article is being written [see box on page 62]. The key results have been quickly reproduced in over a dozen laboratories, some of which have applied alternative procedures of verification as well. Because fullerenes are readily soluble and vaporizable molecules that remain stable in air, they are perfectly suited to a wide range of techniques.

One of the most powerful techniques—nuclear magnetic resonance (NMR)—has confirmed the single most critical aspect of the soccerball structure: that all 60 carbon atoms have exactly the same relation to the whole. Only the truncated icosahedral structure we proposed for C_{60} arranges the atoms so symmetrically as to distribute the strain of closure equally. Such even distribution makes for great strength and stability. Indeed, that is why we proposed the structure in the first place: it explains the extraordinary stability of the 60-atom species.

Because C_{60} is the most symmetric molecule possible in three-dimensional Euclidean space, it is literally the roundest of round molecules. Edgeless, chargeless and unbound, the molecule spins freely, as NMR experiments show.

more than 100 million times a secon... The NMR experiments also dramatically verify that C_{70} has the shape of a tiny rugby ball: at room temperature. It spins rapidly about its long axis, stopping its frantic motion only below the temperature of liquid air.

High-resolution electron microscopy revealed these little carbon balls one at a time—as predicted, they spanned a bit more than one nanometer (a billionth of a meter). Scanning tunneling microscopy showed that when C_{60} molecules are deposited on a crystalline surface, they pack as regularly as billiard balls. X-ray diffraction studies demonstrated that—as one would expect—C_{60} crystallizes in a face-centered cubic lattice, with the balls a little more than 10 angstroms apart [see illustration on page 62]. The crystals are as soft as graphite. When squeezed to less than 70 percent of their initial volume, calculations predict that they will become even harder than diamond. When the pressure is relieved, they are observed to spring back to their normal volume. Thrown against steel surfaces at speeds somewhat greater than 17,000 miles per hour (about the orbital speed of the U.S. space shuttle), they are incredibly resilient: they just bounce back.

We found that the most convenient way to generate fullerenes consists of setting up an arc between two graphite electrodes. We maintained a constant gap by screwing the electrodes toward each other as fast as their tips evaporated. The process worked best when the helium pressure was optimized and other gases, such as hydrogen and water vapor, were rigorously eliminated. Such measures produced yields of dissolvable fullerenes that typically ranged between 10 and 20 percent of the vaporized carbon. Yields as high as 45 percent have recently been reported.

The only irreducible cost appears to be that of the electricity needed to run the arc. But even the small bench-top generators we are now using in our laboratory provide electricity at a cost that amounts to only about five cents per gram of C_{60}. Recently it has been found that a sooting flame (such as that of a candle) can be used to produce substantial yields of C_{60}. In the long run, this may prove the cheapest way to make the material. When the first large-scale applications of fullerenes are found—perhaps in superconductors, batteries or microelectronics [see box on page 62]—the manufacturing cost of C_{60} will probably fall close to that of aluminum: a few dollars a pound. What had recently been described as the "most controversial molecule in the

"Cosmos" is well on its way to becoming a bulk commodity.

A host of questions arises out of this wonder. What exactly is the helium doing? How can such a perfectly symmetric molecule be formed with such high efficiency out of the chaos of a carbon arc? And, on a more personal level, where did we go wrong? Why did we, and all other chemists for that matter, fail in the search for the yellow vial? Our technique involved helium as well. What did the Krätschmer-Huffman team do that made such a big difference?
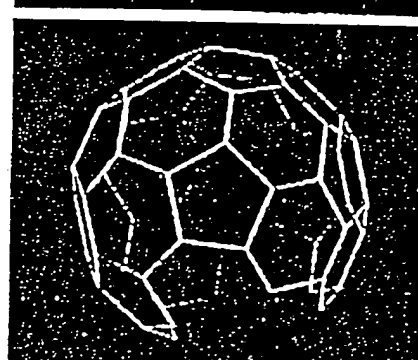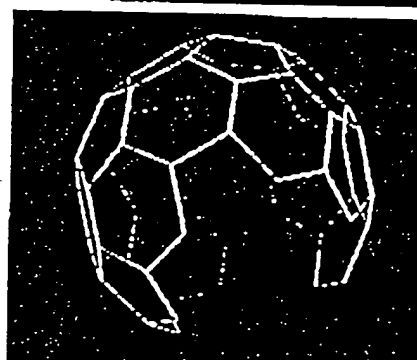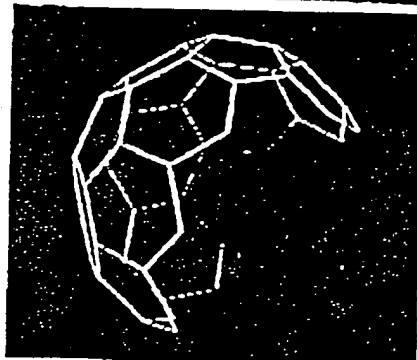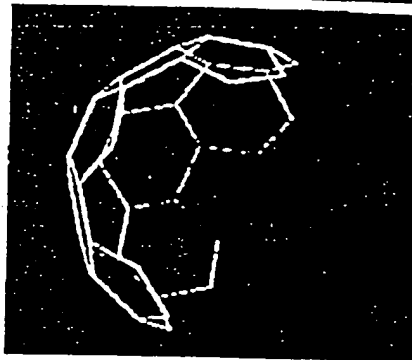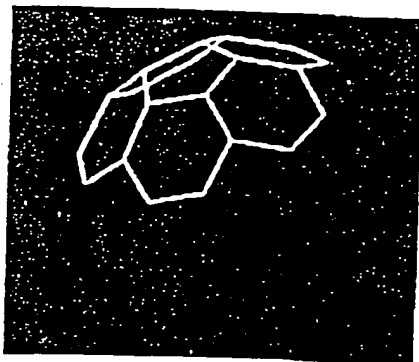
We now believe the answers to these questions lie in the way carbon vapor condenses at high temperatures. Linear carbon chains appear to link together to form graphitic sheets, and the sheets anneal as they grow in the hot vapor. Finally, stable, cagelike structures are favored by a key concept, which we call the pentagon rule.

Scientists had long known that when carbon is vaporized, most of its atoms initially coalesce into clusters ranging from two to 15 atoms or so. The very smallest carbon molecules are known to prefer essentially one-dimensional geometries. But clusters containing at least 10 atoms most commonly form a monocyclic ring—a kind of molecular Hula-Hoop that is especially favored at low temperatures. At very high temperatures, the rings break open to form units that comprise as many as 25 carbon atoms, taking the form of linear chains. Such chains might be imagined to look something like writhing snakes as they vibrate in the hot vapor.

It was these linear carbon chains that initially got us involved in carbon cluster studies and led to the discovery of C_{60}. Our British colleague, Harry Kroto, had theorized that the great abundance of such linear carbon chains in interstellar space may arise from chemical reactions in the outer atmospheres of carbon-rich red giant stars. In the early 1980s one of us (Smalley) had developed a supersonic cluster-beam device for the general study of small clusters composed of essentially any element in the periodic table [see "Microclusters," by Michael A. Duncan and Dennis H. Rouvray; SCIENTIFIC AMERICAN, December 1989].

We produced clusters by focusing an intense pulsed laser on a solid disk of the element to be studied. The local temperature could readily be brought above 10,000 degrees C—hotter than the surface of most stars and certainly hot enough to vaporize any known material. The resulting vapor was entrained in a powerful gust of helium, a chemi-

cally inert carrier gas, which cooled vapor so that it could condense into small clusters. As the carrier gas expanded through a nozzle into a vacuum, it generated a supersonic beam of clusters whose sizes could be measured by a mass spectrometer.

In 1984 a group at Exxon using a copy of the cluster-beam apparatus developed at Rice had been the first to study carbon clusters in this fashion. Their results strongly suggested that the linear carbon chains Kroto wanted to study were in fact being produced in abundance. In addition, they reported a bizarre pattern among the larger clusters: the distribution was strikingly lacking in the species having an odd number of atoms.

The Exxon researchers recorded but did not notice that two particular even-numbered members, C_{60} and C_{70}, were somewhat more abundant than their neighbors [see bottom illustration on page 58]. The mysterious even-numbered distribution of clusters was separated from the small linear-chain distribution by what appeared to be something of a forbidden zone—a region of clusters between roughly 25 and 35 atoms in size in which few if any clusters could be detected.

The even-numbered distribution was soon discovered to result from the fullerenes. In one of our many studies of Kroto's linear carbon chains, we reproduced the Exxon results but found something quite striking about the distribution of large, even-numbered clusters. Heath, Kroto and O'Brien noticed that the 60th cluster seemed five times more abundant than any other even-numbered cluster in the range between 50 and 70 atoms. This differential was dramatically greater than anything that had been seen before.

After much discussion, Heath and O'Brien spent the next weekend playing with the conditions in the laser-vaporization machine's supersonic nozzle. By Monday morning they had managed to find conditions in which C_{60} stood out in the cluster distribution like a flagpole. By the next morning we had had our Eureka! experience, and we were playing with every sort of soccerball we could get our hands on.

We found that we could explain the dominance of the even-numbered clusters by assuming they had all taken the structure of hollow, geodesic domes. They were all fullerenes. We could also argue that some fullerenes were more abundant than others because of the smoothness of the clusters' surface and the natural grouping of pentagons.

Pentagons provided an important clue. Although hundreds of examples are known in chemistry of five-membered rings attached to six-membered rings in stable aromatic compounds (for example, the nucleic acids adenine and guanine), only a few occur whose two five-membered rings share an edge. Interestingly, the smallest fullerene in which pentagons need not share an edge is C_{60}; the next is C_{70}. Although C_{72} and all larger fullerenes can easily adopt structures in which the five-membered rings are well separated, one finds that these pentagons in the larger fullerenes occupy strained posi-

tio. This vulnerability makes the carbon atoms at such sites particularly susceptible to chemical attack.

The big question, however, was not why fullerenes were stable but rather how they formed so readily in laser-vaporized graphite. Near the end of 1985, we suggested that the process began with linear chains. As the carbon vapor began to condense, the linear chains would grow long enough to flip back on themselves to form large monocyclic Hula-Hoops. As the growth continued, the chains would also fold into more effectively connected polycyclic network structures. Because graphite,

COLOR OF C_{60} depends on its form. This yellow film was sublimed onto a glass window that had been bolted to a vacuum oven. The benzene solution is magenta.
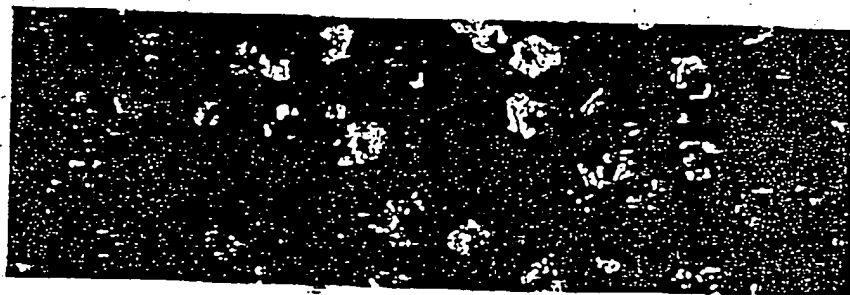
FULLERENE CRYSTALS were produced by evaporating a benzene solution of C_{60} containing a significant admixture of C_{70}.
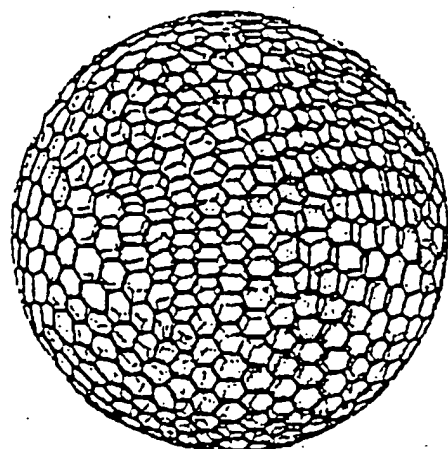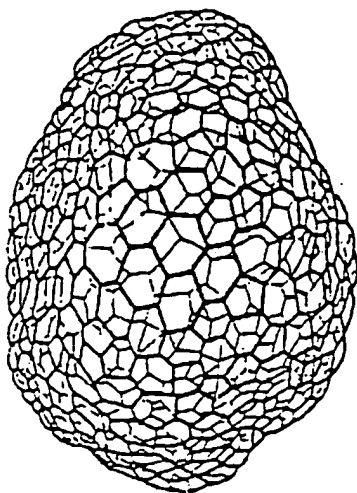
graphitic sheet structures as flat. After all, the sheets are certainly flat in a perfect crystal of graphite, and there is a huge class of very stable polycyclic aromatic hydrocarbons that are also flat (naphthalene and anthracene, for instance). But these free-floating graphitic sheets in the condensing carbon vapor have no atoms to tie up the dangling bonds on their edges. They therefore have little reason to remain flat. Indeed, the physical tendency to reach the lowest energy level available induces the sheets to eliminate their dangling bonds by curling up.

We discovered a strategy—the pentagon rule—according to which the sheets could accomplish this feat. The sheets rearrange their bonding so that pentagons are formed, causing the network to curve and permitting at least one good carbon-carbon bond to replace two dangling bonds. If some pentagons were good, more would be better. But we cautioned that it would be wise to avoid having two pentagons positioned so that they shared an edge, since this configuration is known to be rather unstable. If this process continues as the graphitic sheet grows, the network will naturally curl until the opposing edges meet to form the perfect soccerball structure. In this way, we argued in 1985, the formation of buckminsterfullerene from spontaneously condensing carbon vapor might not be so surprising after all.

Of course, there is no reason to expect that all growing graphitic sheets will close up—they merely have a theoretical propensity to do so. In reality, we expected clusters to grow too fast for imperfections to be corrected, so that the growing edge would typically overrun the opposite side, much like an overgrown toenail. Further growth would result in a spiraling nautilus-shaped structure that would prevent the growing edge from ever meeting its opposite, which would be hopelessly buried on the inside of the spiral.

This spiral shape seemed so interesting that we went on to suggest it may be formed in sooting flames and may in fact be the nucleus involved in the formation of soot. In this scenario, fullerenes like C_{60} and C_{70} are rather unlikely local stopping points in a curving, spiraling growth mechanism that ultimately results in soot.

Although this turned out to be a useful model, which within a few years led to the discovery that C_{60} and the other fullerenes are in fact abundant in all sooting flames, to some extent it misled us. Perfect closure need not always be that unlikely. Granted, the curving process is liable to be waylaid in a can-

dle flame, where much hydrogen wanders around, tying up dangling bonds as it goes. These terminated dangling bonds would tend to frustrate the curving and closing mechanism.

But in a pure condensing carbon vapor one may be able to prolong the period in which the carbon nets remain open. If the temperature is kept high enough, the nets will effectively anneal, that is, they will adopt their most favored form by obeying the pentagon rule. Such conditions should thus produce a very high yield of C_{60}. This is what we believe Krätschmer and Huffman achieved. By using a simple, resistively heated graphite rod, they ensured that the concentration of small linear carbon radicals would be low and that the graphitic sheets would add these chains to their edges relatively slowly. The helium was critical, we believe, because it slowed migration of these chains away from the graphite rod. More chains lingered near the arc, which provided the heat they needed to continue to curve.

Not only was this line of reasoning available to us in 1985, it was a direct extension of the growth model we proposed at the time. Yet the yellow vial, so close to our grasp, eluded us because we did not think big. We were so intent on proving the existence of soccerball molecules that we asked no more of our model than that it rationalize tiny yields of C_{60}. Had we asked for more, had we considered the model's logical consequences, we would have—at least we should have—realized that we were heating and cooling the carbon too fast for it to anneal properly.

The solution would then have become obvious: the whole apparatus must be

heated so that the laser-vaporized carbon plume expands further while it is still hot enough to anneal. Sure enough, when we finally did this in November 1990 by keeping the graphite target in an oven at 1,200 degrees C while passing helium over it slowly, a yellow-brown film of C_{60} and C_{70} rapidly sublimed on the surface of the oven. We found what we were looking for—five years late.

It appears, therefore, that a rather simple model explains the ready formation of this brand-new class of carbon molecules. Amazingly, C_{60} appears to result inevitably when carbon condenses slowly enough and at a high enough temperature. This discovery has come a bit later than it should have. But no matter: now we have it. And now the real fun can begin!

FURTHER READING

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GREAT BALLS OF CARBON: THE STORY OF BUCKMINSTERFULLERENE. Richard E. Smalley in The Sciences, Vol. 31, No. 2, pages 22-28; March/April 1991.

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FULLERENES C_{60} AND C_{70} IN FLAMES. Jack B. Howard, J. Thomas McKinnon, Yakov Makarovsky, Arthur L. Lafleur and M. Elaine Johnson in Nature, Vol. 352, No. 6331, pages 139-141; July 11, 1991.

the most stable known form of carbon, has its atoms bound in infinite hexagonal sheets, we suspected that the polycyclic network clusters resembled pieces of such sheets. We expected it to look like a fragment of chicken wire.

Like a cutout section of chicken wire, these graphitic sheets would have many dangling bonds, making them chemically reactive—much more so than the smaller linear chains, which have only two such bonds, one on each end. The sheets, therefore, would not be expected to be abundant in the cluster beams.

Almost as soon as they form, they react with other small carbon molecules and grow too large to be seen. This, we believe, explains why there is a forbidden zone between the small linear-chain distribution and the first small fullerenes.

Chemists are conditioned to think of

Fullerene Electronics

Currently the most technologically interesting properties of bulk C_{60} are electronic: In various compound forms it functions as an insulator, a conductor, a semiconductor and a superconductor.

The material crystallizes when C_{60} molecules pack together like Ping-Pong balls in a face-centered cubic lattice. Calculations over the past few months have predicted that this new material is a direct band-gap semiconductor like gallium arsenide. All its units stand precisely at their posts in a crystalline structure. But unlike the elements of gallium arsenide, the buckyballs spin freely and at random. This disorder gives them a certain resemblance to amorphous silicon—a constituent of inexpensive solar cells. The peculiar disorder within order of bulk C_{60} has yet to be fully explored, but it is expected to produce a wholly new kind of semiconductor.

Early in 1991 researchers at AT&T Bell Laboratories discovered that they could mix, or dope, C_{60} with potassium to produce a new metallic phase—a "buckide" salt. It reaches its maximum electrical conductivity when there are three potassium atoms to each buckyball. If too much potassium is added, however, the material becomes insulating. Subsequent work has shown that K_3C_{60} is a stable metallic crystal consisting of a face-centered cubic structure of buckyballs, with potassium ions filling the cavities between the balls. Potassium buckide is the first completely three-dimensional molecular metal.

The Bell Labs team further discovered that this K_3C_{60} metal becomes a superconductor when cooled below 18 kelvins. When rubidium is substituted for the potassium, the critical temperature for superconductivity was found to be near 30 kelvins. (Recently workers at Allied-Signal, Inc., detected superconductivity at 43 kelvins for rubidium-thallium–doped material.) Careful work at the University of California at Los Angeles has shown that the superconducting phase is stable and readily annealed—imperfections can be smoothed away by heating and cooling.

The material can therefore be manufactured as a three-dimensional superconductor, making it a candidate for practical superconducting wires. Early estimates of magnetic and other characteristics indicate that these superconducting buckide salts are similar to the high-temperature superconducting ceramics made of yttrium, barium and copper oxide.

Recent work at the University of Minnesota has shown that highly ordered C_{60} films can readily be grown on crystalline substrates, such as gallium arsenide. This attribute makes the film a suitable material for microelectronic fabrication. Beautifully regular films of the K_3C_{60} superconductor can also be made [see micrograph at right], and the interface between the C_{60} crystalline film and the K_3C_{60} material has been found to be stable. It may thus lend itself to the production of intricately layered microelectronic devices.

In order for the semiconducting properties of fullerene materials to be thoroughly exploited, scientists need to learn how to dope them selectively to make n-type and p-type fullerene films, which donate electrons and holes, respectively. Such doping may involve putting a dopant atom inside the cage, either by growing the cage around the atom or by shooting atoms through the carbon walls by brute force. Small atoms, such as helium, have already been injected this way into the C_{60} cage, and it seems likely that hydrogen and lithium are insertable as well.

The versatility of bulk C_{60} seems to grow week by week. As we go to press, for example, there is a report suggesting that fullerene complexes exhibit ferromagnetic qualities in the absence of metals, an unparelleled phenomenon. Also, British workers from the universities of Leicester, Southampton and Sussex have just reported the generation of macroscopic quantities of fully fluorinated buckyballs ($C_{60}F_{60}$). The resulting "teflon balls" may be among the world's best lubricants. We do not know what the fullerenes' burgeoning traits will allow, but it would be surprising if the possibilities are not wonderful.
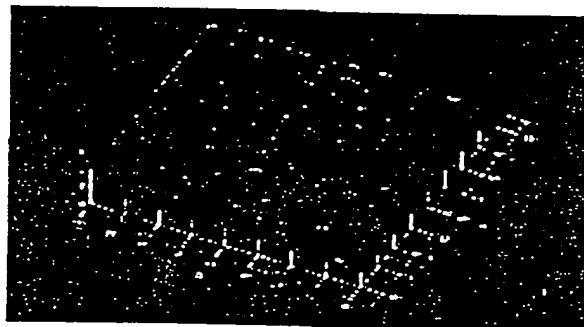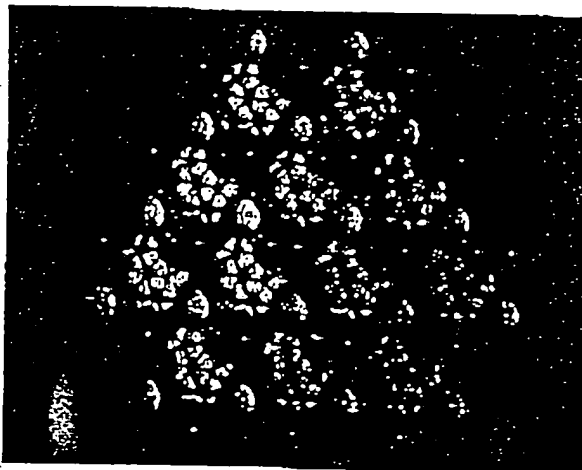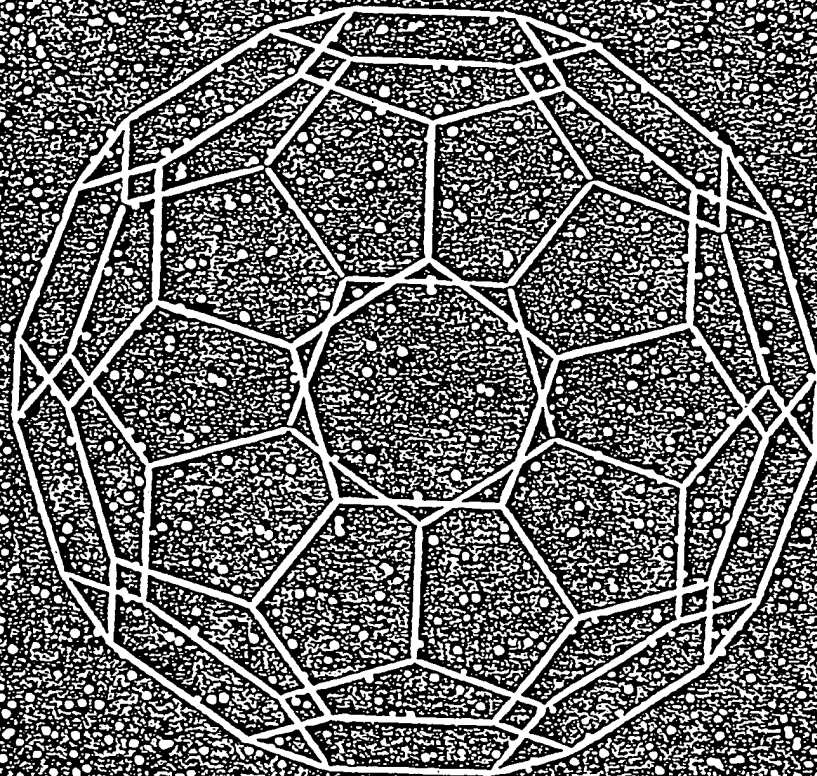

SUPERCONDUCTING FULLERIDE forms when buckyballs are doped with potassium in the ratio of K_3C_{60} (diagram), producing a crystal that can be grown on a gallium arsenide substrate (scanning tunneling micrograph).

SIXTY-CARBON CLUSTER

AUTUMN BOOKS

Harvey Brooks
(transformation of MIT)

P. N. Johnson-Laird
(brain and mind)

Anthony W. Clare
(psychoanalysis as religion)

A. O. Lucas
(war on disease)

Hendrik B. G. Casimir
(physics and physicists)

Gordon Thompson
(dimensions of nuclear proliferation)

Jacques Ninio
(origins of life)

Edward Harrison
(steps through the cosmos)

C60: Buckminsterfullerene

H. W. Kroto[*], J. R. Heath, S. C. O'Brien, R. F. Curl
& R. E. Smalley

Rice Quantum Institute and Departments of Chemistry and Electrical
Engineering, Rice University, Houston, Texas 77251, USA

During experiments aimed at understanding the mechanisms by
which long-chain carbon molecules are formed in interstellar space
and circumstellar shells[1], graphite has been vaporized by laser
irradiation, producing a remarkably stable cluster consisting of
60 carbon atoms. Concerning the question of what kind of 60-
carbon atom structure might give rise to a superstable species, we
suggest a truncated icosahedron, a polygon with 60 vertices and
32 faces, 12 of which are pentagonal and 20 hexagonal. This object
is commonly encountered as the football shown in Fig. 1. The C_{60}
molecule which results when a carbon atom is placed at each vertex
of this structure has all valences satisfied by two single bonds and
one double bond, has many resonance structures, and appears to
be aromatic.

The technique used to produce and detect this unusual
molecule involves the vaporization of carbon species from the
surface of a solid disk of graphite into a high-density helium
flow using a focused pulsed laser. The vaporization laser was
the second harmonic of Q-switched Nd:YAG producing pulse
energies of ~30 mJ. The resulting carbon clusters were expanded
in a supersonic molecular beam, photoionized using an excimer
laser, and detected by time-of-flight mass spectrometry. The
vaporization chamber is shown in Fig. 2. In the experiment the
pulsed valve was opened first and then the vaporization laser
was fired after a precisely controlled delay. Carbon species were
vaporized into the helium stream, cooled and partially equili-
brated in the expansion, and travelled in the resulting molecular
beam to the ionization region. The clusters were ionized by
direct one-photon excitation with a carefully synchronized
excimer laser pulse. The apparatus has been fully described
previously[2-5].

The vaporization of carbon has been studied previously in a
very similar apparatus[6]. In that work clusters of up to 190 carbon
atoms were observed and it was noted that for clusters of more
than 40 atoms, only those containing an even number of atoms
were observed. In the mass spectra displayed in ref. 6, the C_{60}
peak is the largest for cluster sizes of >40 atoms, but it is not
completely dominant. We have recently re-examined this system
and found that under certain clustering conditions the C_{60} peak
can be made about 40 times larger than neighbouring clusters.

Figure 3 shows a series of cluster distributions resulting from
variations in the vaporization conditions evolving from a cluster
distribution similar to that observed in ref. 3, to one in which
C_{60} is totally dominant. In Fig. 3c, where the firing of the vaporiz-
ation laser was delayed until most of the He pulse had passed,
a roughly gaussian distribution of large, even-numbered clusters
with 38-120 atoms resulted. The C_{60} peak was largest but not
dominant. In Fig. 3b, the vaporization laser was fired at the time
of maximum helium density; the C_{60} peak grew into a feature
perhaps five times stronger than its neighbours, with the excep-
tion of C_{70}. In Fig. 3a, the conditions were similar to those in
Fig. 3b but in addition the integrating cup depicted in Fig. 2
was added to increase the time between vaporization and
expansion. The resulting cluster distribution is completely domi-
nated by C_{60}, in fact more than 50% of the total large cluster
abundance is accounted for by C_{60}; the C_{70} peak has diminished
in relative intensity compared with C_{60}, but remains rather
prominent, accounting for ~5% of the large cluster population.

Our rationalization of these results is that in the laser vaporiz-
ation, fragments are torn from the surface as pieces of the planar

Fig. 1 A football (in the
United States, a soccerball)
on Texas grass. The C_{60}
molecule featured in this
letter is suggested to have
the truncated icosahedral
structure formed by
replacing each vertex on the
seams of such a ball by a
carbon atom.
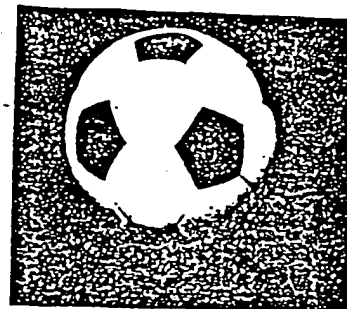
graphite fused six-membered ring structure. We believe that the
distribution in Fig. 3c is fairly representative of the nascent
distribution of larger ring fragments. When these hot ring clusters
are left in contact with high-density helium, the clusters equili-
brate by two- and three-body collisions towards the most stable
species, which appears to be a unique cluster containing 60
atoms.

When one thinks in terms of the many fused-ring isomers
with unsatisfied valences at the edges that would naturally arise
from a graphite fragmentation, this result seems impossible:
there is not much to choose between such isomers in terms of
stability. If one tries to shift to a tetrahedral diamond structure,
the entire surface of the cluster will be covered with unsatisfied
valences. Thus a search was made for some other plausible
structure which would satisfy all sp^2 valences. Only a spheroidal
structure appears likely to satisfy this criterion, and thus Buck-
minster Fuller's studies were consulted (see, for example, ref.
7). An unusually beautiful (and probably unique) choice is the
truncated icosahedron depicted in Fig. 1. As mentioned above,
all valences are satisfied with this structure, and the molecule
appears to be aromatic. The structure has the symmetry of the
icosahedral group. The inner and outer surfaces are covered
with a sea of π electrons. The diameter of this C_{60} molecule is
~7 Å, providing an inner cavity which appears to be capable
of holding a variety of atoms[8].

Assuming that our somewhat speculative structure is correct,
there are a number of important ramifications arising from the
existence of such a species. Because of its stability when formed
under the most violent conditions, it may be widely distributed
in the Universe. For example, it may be a major constituent of
circumstellar shells with high carbon content. It is a feasible
constituent of interstellar dust and a possible major site for
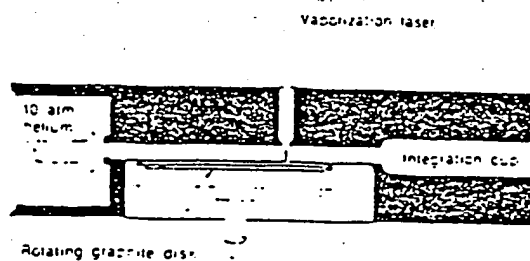

Fig. 2 Schematic diagram of the pulsed supersonic nozzle used
to generate carbon cluster beams. The integrating cup can be
removed at the indicated line. The vaporization laser beam (30-
40 mJ at 532 nm in a 5-ns pulse) is focused through the nozzle,
striking a graphite disk which is rotated slowly to produce a smooth
vaporization surface. The pulsed nozzle passes high-density helium
over this vaporization zone. This helium carrier gas provides the
thermalizing collisions necessary to cool, react and cluster the
species in the vaporized graphite plasma, and the wind necessary
to carry the cluster products through the remainder of the nozzle.
Free expansion of this cluster-laden gas at the end of the nozzle
forms a supersonic beam which is probed 1.3 m downstream with
a time-of-flight mass spectrometer.

44 52 60 68 76 84
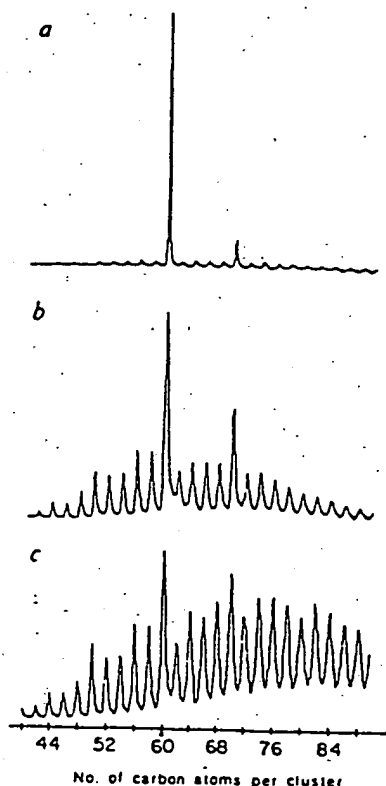
No. of carbon atoms per cluster

Fig. 3 Time-of-flight mass spectra of carbon clusters prepared by laser vaporization of graphite and cooled in a supersonic beam. Ionization was effected by direct one-photon excitation with an ArF excimer laser (6.4 eV, 1 mJ cm^{-2}). The three spectra shown differ in the extent of helium collisions occurring in the supersonic nozzle. In c, the effective helium density over the graphite target was less than 10 torr—the observed cluster distribution here is believed to be due simply to pieces of the graphite sheet ejected in the primary vaporization process. The spectrum in b was obtained when roughly 760 torr helium was present over the graphite target at the time of laser vaporization. The enhancement of C_{60} and C_{70} is believed to be due to gas-phase reactions at these higher clustering conditions. The spectrum in a was obtained by maximizing these cluster thermalization and cluster–cluster reactions in the 'integration cup' shown in Fig. 2. The concentration of cluster species in the especially stable C_{60} form is the prime experimental observation of this study.

surface-catalysed chemical processes which lead to the formation of interstellar molecules. Even more speculatively, C_{60} or a derivative might be the carrier of the diffuse interstellar lines[9].

If a large-scale synthetic route to this C_{60} species can be found, the chemical and practical value of the substance may prove extremely high. One can readily conceive of C_{60} derivatives of many kinds—such as C_{60} transition metal compounds, for example, C_{60}Fe or halogenated species like $C_{60}F_{60}$ which might be a super-lubricant. We also have evidence that an atom (such as lanthanum[8] and oxygen[1]) can be placed in the interior, producing molecules which may exhibit unusual properties. For example, the chemical shift in the NMR of the central atom should be remarkable because of the ring currents. If stable in macroscopic, condensed phases, this C_{60} species would provide a topologically novel aromatic nucleus for new branches of organic and inorganic chemistry. Finally, this especially stable and symmetrical carbon structure provides a possible catalyst and/or intermediate to be considered in modelling prebiotic chemistry.

We are disturbed at the number of letters and syllables in the rather fanciful but highly appropriate name we have chosen in the title to refer to this C_{60} species. For such a unique and centrally important molecular structure, a more concise name would be useful. A number of alternatives come to mind (for example, ballene, spherene, soccerene, carbosoccer), but we prefer to let this issue of nomenclature be settled by consensus.

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9. Herbig, E. Astrophys. J. 196, 129-160 (1975).

The Nobel Prize in Chemistry 1996

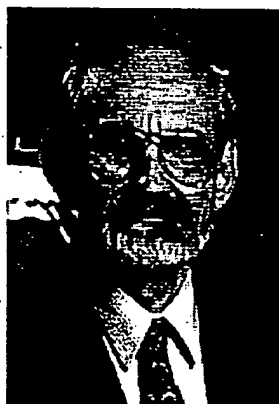"for their discovery of fullerenes"

Press release

The Fullerene Gallery

Robert F. Curl, Jr.

USA

Rice University
Houston, USA

1933 -

Autobiography

Sir Harold W. Kroto

U.K.

University of Sussex,
Brighton, U.K.

1939 -

Autobiography

Richard E. Smalley

USA

Rice University,
Houston, USA

1943 -

Autobiography

Press Release: The 1996 Nobel Prize in Chemistry

KUNGL. VETENSKAPSAKADEMIEN
THE ROYAL SWEDISH ACADEMY OF SCIENCES

9 October 1996

The Royal Swedish Academy of Sciences has decided to award the 1996 Nobel Prize in Chemistry to

Professor **Robert F. Curl, Jr.**, Rice University, Houston, USA,
Professor **Sir Harold W. Kroto**, University of Sussex, Brighton, U.K., and
Professor **Richard E. Smalley**, Rice University, Houston, USA,

for their discovery of fullerenes.

Note: This document is made for Netscape 2.0 or later, and some of the chemical formulas might not appear as intended using other browsers.

The discovery of carbon atoms bound in the form of a ball is rewarded

New forms of the element carbon - called fullerenes - in which the atoms are arranged in closed shells was discovered in 1985 by **Robert F. Curl, Harold W. Kroto** and **Richard E. Smalley**. The number of carbon atoms in the shell can vary, and for this reason numerous new carbon structures have become known. Formerly, six crystalline forms of the element carbon were known, namely two kinds of graphite, two kinds of diamond, chaoit and carbon(VI). The latter two were discovered in 1968 and 1972.

Fullerenes are formed when vaporised carbon condenses in an atmosphere of inert gas. The gaseous carbon is obtained e.g. by directing an intense pulse of laser light at a carbon surface. The released carbon atoms are mixed with a stream of helium gas and combine to form clusters of some few up to hundreds of atoms. The gas is then led into a vacuum chamber where it expands and is cooled to some degrees above absolute zero. The carbon clusters can then be analysed with mass spectrometry.

Curl, Kroto and Smalley performed this experiment together with graduate students J.R. Heath and S.C. OBrien during a period of eleven days in 1985. By fine-tuning the experiment they were able in particular to produce clusters with 60 carbon atoms and clusters with 70. Clusters of 60 carbon atoms, C_{60}, were the most abundant. They found high stability in C_{60}, which suggested a molecular structure of great symmetry. It was suggested that C_{60} could be a "truncated icosahedron cage", a polyhedron with 20 hexagonal (6-angled) surfaces and 12 pentagonal (5-angled) surfaces. The pattern of a European football has exactly this structure, as does the geodetic dome designed by the American architect R. Buckminster Fuller for the 1967 Montreal World Exhibition. The researchers named the newly-discovered structure *buckminsterfullerene* after him.

The discovery of the unique structure of the C_{60} was published in the journal *Nature* and had a mixed reception - both criticism and enthusiastic acceptance. No physicist or chemist had expected that carbon would be found in such a symmetrical form other than those already known. Continuing their work during 1985-90, Curl, Kroto and Smalley obtained further evidence that the proposed structure ought to be correct. Among other things they succeeded in identifying carbon clusters that enclosed one or more metal atoms. In 1990 physicists W. Krätschmer and D.R. Huffman for the first time produced isolable quantities of C_{60} by causing an arc between two graphite rods to burn in a helium atmosphere and extracting the carbon condensate so formed using an organic solvent. They obtained a mixture of C_{60} and C_{70}, the structures of which could be determined. This confirmed the correctness of the C_{60} hypothesis. The way was thus open for studying the chemical properties of C_{60} and other carbon clusters such as C_{70}, C_{76}, C_{78} and C_{84}. New substances were produced from these compounds, with new and unexpected properties. An entirely new branch of chemistry developed, with consequences in such diverse areas as astrochemistry, superconductivity and materials chemistry/physics.

Background
Many widely diverse research areas coincide in the discovery of the fullerenes. **Harold W. Kroto** was at the time active in microwave spectroscopy, a science which thanks to the growth of radioastronomy can be used for analysing gas in space, both in stellar atmospheres and in interstellar gas clouds. Kroto was particularly interested in carbon-rich giant stars. He had discovered and investigated spectrum lines in their atmospheres and found that they could be ascribed to a kind of long-chained molecule of only carbon and nitrogen, termed cyanopolyynes. The same sort of molecules is also found in interstellar gas clouds. Kroto's idea was that these carbon compounds had been formed in stellar atmospheres, not in clouds. He now wished to study the formation of these long-chain molecules more closely.

He got in touch with **Richard E. Smalley**, whose research was in cluster chemistry, an important part of chemical physics. A cluster is an aggregate of atoms or molecules, something in between microscopic particles and macroscopic particles. Smalley had designed and built a special *laser-supersonic cluster beam apparatus* able to vaporise almost any known material into a plasma of atoms and study the design and distribution of the clusters. His paramount interest was clusters of metal atoms, e.g. metals included in semiconductors, and he often performed these investigations together with **Robert F. Curl**, whose background was in microwave and infra-red spectroscopy.

Atoms form clusters
When atoms in a gas phase condense to form clusters, a series is formed where the size of the clusters varies from a few atoms to many hundreds. There are normally two size maxima visible in the distribution curve, one around small clusters and one around large. It is often found that cer-tain cluster sizes may dominate, and the number of atoms in these is termed a "magic number", a term borrowed from nuclear physics. These dominant cluster sizes were assumed to have some special property such as high symmetry.

Fruitful contact
Through his acquaintanceship with Robert Curl, Kroto learned that it should be possible to use Smalley's instrument to study the vaporisation and cluster formation of carbon, which might afford him evidence that the long-carbon-chain compounds could have been formed in the hot parts of stellar atmospheres. Curl conveyed this interest to Smalley and the result was that on 1 September 1985 Kroto arrived in Smalley's laboratory to start, together with Curl and Smalley, the experiments on carbon vaporisation. In the course of the work it proved possible to influence drastically the size distribution of the carbon clusters where, predominantly, 60 appeared as a magic number but also 70 (Fig. 1). The research group

now got something else to think about. Instead of long carbon chains, the idea arose that the C_{60} cluster could have the structure of a truncated (cut off) icosahedron (Fig. 2) since its great stability was assumed to correspond to a closed shell with a highly symmetrical structure. C_{60} was given a fanciful name, buckminsterfullerene, after the American architect R. Buckminster Fuller, inventor of the geodesic dome. This hectic period ended on 12 September with the despatch of a manuscript entitled C_{60}: *Buckminsterfullerene* to *Nature*. The journal received it on 13 September and published the article on 14 November 1985.

Sensational news
For chemists the proposed structure was uniquely beautiful and satisfying. It corresponds to an aromatic, three-dimensional system in which single and double bonds alternated, and was thus of great theoretical significance. Here, moreover, was an entirely new example from a different research tradition with roots in organic chemistry: producing highly symmetrical molecules so as to study their properties. The Platonic bodies have often served as patterns, and hydrocarbons had already been synthesised as tetrahedral, cubic or dodecahedral (12-sided) structures.

Carbon atoms per cluster

Fig. 1
Using mass spectroscopy it was found that the size distribution of carbon clusters could be drastically affected by increasing the degree of chemical "boiling" in the inlet nozzle to the vacuum chamber. Clusters with 60 and 70 carbon atoms could be produced. (Acc. Chem. Res., Vol. 25, No. 3, 1992)

Fig. 2
Models of the structures of C_{60}. (Acc. Chem. Res., Vol. 25, No. 3, 1992)

Further investigations

To gain further clarity Curl, Kroto and Smalley continued their investigations of C_{60}. They attempted to make it react with other compounds. Gases such as hydrogen, nitrous oxide, carbon monoxide, sulphur dioxide, oxygen or ammonia were injected into the gas stream, but no effect on the C_{60} peak recorded in the mass spectrometer could be demonstrated. This showed that C_{60} was a slow-reacting compound. It also turned out that all carbon clusters with an even number of carbon atoms from 40-80 (the interval that could be studied) reacted equally slowly. Analogously with C_{60} all these should then correspond to entirely closed structures, resembling cages. This was in agreement with Euler's law, a mathematical proposition which states that for any polygon with n edges, where n is an even number greater than 22, at least one polyhedron can be constructed with 12 pentagons and $(n-20)/2$ hexagons, which, in simple terms, states that it is possible with 12 pentagons and with none or more than one hexagon to construct a polyhedron. For large n many different closed structures can occur, thus also for C_{60}, and it was presumably the beautiful symmetry of the proposed structure that gave it the preference.

The combination of chemical inertia in clusters with even numbers of carbon atoms and the possibility that all these could possess closed structures in accordance with Euler's law, led to the proposal that all these carbon clusters should have closed structures. They were given the name fullerenes and conceivably an almost infinite number of fullerenes could exist. The element carbon had thus assumed an almost infinite number of different structures.

C_{60} and metals

New experiments were rapidly devised to test the C_{60} hypothesis. Since the C_{60} structure is hollow, with room for one or more other atoms, attempts were made to enclose a metal atom. A graphite sheet was soaked with a solution of a metal salt (lanthanum chloride, $LaCl_3$) and subjected to vaporisation-condensation experiments. Masspectroscopic analysis of the clusters formed showed the presence of $C_{60}La^+$. These proved to be photoresistant, i.e. irradiation with intense laser light did not remove the metal atoms. This reinforced the idea that metal atoms were captured inside the cage structure.

The possibility of producing clusters with a metal atom enclosed gave rise to what was termed the "shrink-wrapping" experiment. Ions of one and the same size or at least similar sizes were gathered in a magnetic trap and subjected to a laser pulse. It then turned out that the laser beam caused the carbon cage to shrink by 2 carbon atoms at a time: at a certain cage size, when the pressure on the metal atom inside

became too great, the fragmentation ceased. The shell had then shrunk so that it fitted exactly around the metal atom. For $C_{60}Cs^+$ this size was at $C_{48}Cs^+$, for $C_{60}K^+$ it was at $C_{44}K^+$ and for C_{60}^+ at C_{32}^+.

Further strong evidence gave rise to new chemistry

At the end of the 1980s, strong evidence was available that the C_{60} hypothesis was correct. In 1990 the synthesis of macroscopic quantities of C_{60} through carbon arc vaporisation between two graphite electrodes permitted the attainment of full certainty - the whole battery of methods for structure determination could be applied to C_{60} and other fullerenes and completely confirmed the fullerene hypothesis. As opposed to the other forms of carbon the fullerenes represent well-defined chemical compounds with in some respects new properties. A whole new chemistry has developed to manipulate the fullerene structure, and the properties of fullerenes can be studied systematically. It is possible to produce superconducting salts of C_{60}, new three-dimensional polymers, new catalysts, new materials and electrical and optical properties, sensors, and so on. In addition, it has been possible to produce thin tubes with closed ends, nanotubes, arranged in the same way as fullerenes. From a theoretical viewpoint, the discovery of the fullerenes has influenced our conception of such widely separated scientific problems as the galactic carbon cycle and classical aromaticity, a keystone of theoretical chemistry. No practically useful applications have yet been produced, but this is not to be expected as early as six years after macroscopic quantities of fullerenes became available.

Further reading

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Robert F. Curl Jr., was born in 1933 in Alice, Texas, USA: Ph.D. in chemistry in 1957 at University of California, Berkeley, USA. Curl has since 1958 worked at Rice University, where he has been a professor since 1967.

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Rice University
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Sir Harold W. Kroto was born in 1939 in Wisbech, Cambridgeshire, UK. He obtained his Ph.D. in 1964

at the University of Sheffield, UK. In 1967 he moved to the University of Sussex, where he still works. In 1985 he became Professor of Chemistry there and in 1991 Royal Society Research Professor.

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School of Chemistry and Molecular Sciences
University of Sussex
Brighton, Sussex BN1 9QJ, UK

Richard E. Smalley was born in 1943 in Akron, Ohio, USA. Ph.D. in chemistry 1973 at Princeton University, USA. Professor of Chemistry at Rice University since 1981 and also Professor of Physics at the same university since 1990. Member of the National Academy of Sciences in the USA and other bodies.

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